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XXIII. *The Early Stages of a Submarine Explosion.*
By H. LAMB, F.R.S.*

THE theory of the collapse of a spherical bubble in water has been given by Besant† and Rayleigh‡. The cognate problem of the expansion of a spherical cavity owing to the pressure of an included gas is of some interest as the nearest approach we can make at present to the case of a submarine explosion. The representation is defective in various ways, some of them obvious enough, but the study of the problem as thus idealized may still have some value as indicating at all events the order of magnitude of the results to be expected in certain cases. For very intense explosions the results are subject to considerable qualification, as will appear.

Let us imagine that a quantity of gas is liberated instantaneously in a spherical cavity in an unlimited mass of liquid initially at rest. The liquid is assumed for the present to be incompressible, and the density of the gas at each instant to be uniform. Let R_0 be the initial radius of the cavity, R its radius after a time t , p_0 the initial pressure of the gas, ρ the density of the liquid. The velocity potential

* Communicated by the Author.

† Hydromechanics, p. 198 (1867).

‡ Phil. Mag. vol. xxxiv. p. 94 (1917); Scientific Papers, vol. vi. p. 504.

TABLE I.

$x.$	$c_0 t/R_0.$	$R/R_0.$	$\dot{R}/c_0.$	$R_0^3/R^3.$	$pr/p_0 R_0.$
0	0	1.000	0	1.000	1.000
.1	.090	1.004	.089	.988	.996
.2	.181	1.016	.175	.953	.984
.3	.277	1.037	.257	.897	.965
.4	.378	1.066	.325	.826	.936
.5	.488	1.105	.385	.741	.901
.6	.609	1.155	.432	.649	.858
.7	.745	1.217	.466	.555	.807
.8	.903	1.292	.487	.463	.752
.9	1.087	1.383	.495	.378	.692
1.0	1.330	1.492	.491	.301	.629
1.1	1.578	1.623	.476	.234	.563
1.2	1.915	1.779	.452	.178	.498
1.3	2.343	1.966	.422	.132	.433
1.4	2.899	2.190	.386	.095	.372
1.5	3.634	2.460	.348	.067	.314
1.6	4.627	2.784	.304	.046	.261
1.7	5.996	3.177	.269	.031	.214
1.8	7.919	3.655	.230	.020	.172
1.9	10.68	4.238	.195	.013	.124
2.0	14.72	4.953	.162	.008	.106

whence

$$\frac{\dot{R}^2}{c_0^2} = \frac{2}{3(\gamma-1)} \left\{ \left(\frac{R_0}{R} \right)^3 - \left(\frac{R_0}{R} \right)^{3\gamma} \right\} \dots (16)$$

The maximum of \dot{R} now occurs when

$$(R/R_0)^{3\gamma-3} = \gamma, \quad \dots \dots \dots (17)$$

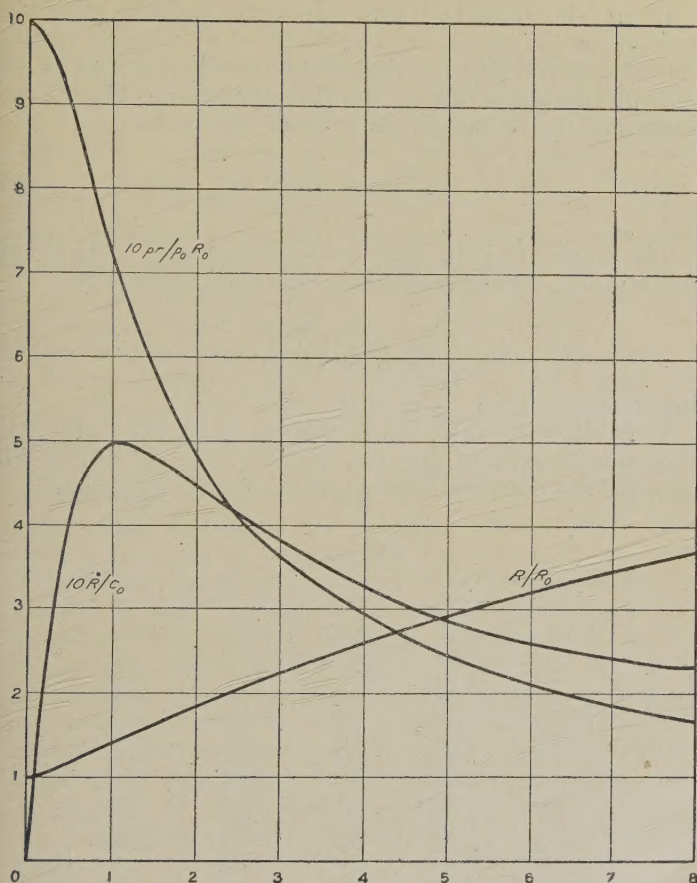
and is given by

$$\frac{\dot{R}^2}{c_0^2} = \frac{2}{3\gamma^{1/(\gamma-1)}} \dots \dots \dots (18)$$

The pressure in the liquid, as found from (2) and (15), is

$$\begin{aligned} \frac{p}{p_0} = & \frac{1}{3(\gamma-1)} \frac{R}{r} \left\{ (3\gamma-4) \left(\frac{R_0}{R} \right)^{3\gamma} + \left(\frac{R_0}{R} \right)^3 \right\} \\ & - \frac{1}{3(\gamma-1)} \frac{R R_0^3}{r^4} \left\{ 1 - \left(\frac{R_0}{R} \right)^{3\gamma-3} \right\}, \quad \dots (19) \end{aligned}$$

the second line being relatively unimportant at a distance from the centre.



The integration of (16) cannot as a rule be effected analytically. An exception worth notice occurs, however, in the case of $\gamma = \frac{4}{3}$. Writing

$$R/R_0 = 1 + z, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (20)$$

we have then

$$(1+z)^2 \frac{dz}{dt} = \frac{c_0}{R_0} \sqrt{2z}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (21)$$

whence

$$\frac{c_0 t}{R_0} = \sqrt{2z} \left(1 + \frac{2}{3}z + \frac{1}{5}z^2\right). \quad . \quad . \quad . \quad (22)$$

It may be remarked that this same formula would be obtained on the isothermal hypothesis if we were to neglect the term depending on the square of the velocity in the general expression (2) for the fluid pressure. The correct isothermal hypothesis gives for *small* values of z

$$\frac{c_0 t}{R_0} = \sqrt{(2z)(1 + \frac{1}{12}z + \dots)}. \quad (23)$$

The maximum of \dot{R} , when $\gamma = \frac{4}{3}$, corresponds to $R/R_0 = \frac{4}{3}$, and is $\cdot 459c_0$. The pressure at a distance is given by

$$\frac{p}{p_0} = \frac{R_0}{r} \left(\frac{R_0}{R} \right)^2, \quad \dots \quad (24)$$

approximately.

The following Table II. is derived from (22) and (24). It is unnecessary to plot the results, since the curves will have the same *general* form as on the former hypothesis.

TABLE II.

R/R_0 .	$c_0 t/R_0$.	\dot{R}/c_0 .	$(R_0/R)^3$.	$pr/p_0 r_0$.
1.0	0	0	1.000	1.000
1.1	.478	.369	.751	.826
1.2	.722	.439	.579	.676
1.3	.943	.458	.455	.592
1.4	1.162	.456	.364	.510
1.5	1.383	.445	.296	.444
1.6	1.612	.428	.244	.391
1.7	1.850	.409	.204	.346
1.8	2.101	.391	.171	.309
1.9	2.364	.372	.146	.277
2.0	2.640	.354	.125	.250
2.1	2.930	.336	.108	.227
2.2	3.235	.320	.094	.207
2.3	3.555	.305	.082	.189
2.4	3.891	.291	.072	.174
2.5	4.244	.277	.064	.160
2.6	4.613	.265	.057	.148
2.7	4.999	.253	.051	.137
2.8	5.404	.242	.046	.128
2.9	5.827	.232	.041	.119
3.0	6.266	.222	.037	.111
4.0	11.76	.153	.016	.063
5.0	19.42	.113	.008	.040

Since cooling of the gas by expansion and consequent diminution of pressure are now taken into account, the

changes take place more slowly than in the previous case.

As a concrete illustration, let us suppose the initial diameter of the cavity to be 1 metre, and the initial pressure p_0 to be 1000 atmospheres. Putting $\rho = 1$, $c_0 = 3.16 \times 10^4$, we find from Table II. that the radius is doubled in $\frac{1}{2.50}$ of a second, and multiplied five-fold in about $\frac{1}{3.0}$ sec. The initial acceleration of the radius is 2.00×10^7 cm./sec.², showing that the neglect of gravity in the early stages of the motion is amply justified. The maximum of \dot{R} occurs when $R = \frac{4}{3}R_0$, $t = .0016$ sec., and is about 145 metres per second, or about one-tenth the velocity of sound in water.

If the initial pressure p_0 had been 10,000 atmospheres, the radius of the cavity would be doubled in about $\frac{1}{7.50}$ sec., and multiplied five-fold in $\frac{1}{10.0}$ sec. The maximum of \dot{R} would now be 460 metres per sec.

A more difficult question remains as to how far the results are modified by the compressibility of the water. It would appear that so long as the velocity which we have denoted by c_0 is small compared with the velocity (c) of sound-waves in the water the effect would not be very great, although the time-scale would be somewhat extended. But with initial pressures of the order of 10,000 atmospheres in our previous example the effect would become appreciable. In the case of a submarine mine the initial pressures may greatly transcend this amount, with the result that the velocities communicated to the adjacent water may exceed the ordinary velocity of sound, even when allowance is made for the diminution of compressibility with increase of pressure. Our theory then ceases to have any very close relation to the facts.

The accurate equations of motion of spherical waves in a compressible medium are easily formulated, although a solution seems at present hopeless. Assuming that p is a definite function of ρ we write

$$\omega = \int_{\rho_1}^{\rho} \frac{dp}{\rho} = \int_{\rho_1}^{\rho} c^2 \frac{d\rho}{\rho}, \quad \dots \dots (25)$$

where ρ_1 is the undisturbed density, and

$$c^2 = dp/d\rho. \quad \dots \dots (26)$$

We have then the dynamical equation

$$\omega = \frac{\partial \phi}{\partial t} - \frac{1}{2}q^2, \quad \dots \dots (27)$$

where q is the velocity, and the kinematical relation

$$\frac{1}{\rho} \frac{D\rho}{Dt} = \nabla^2 \phi. \quad (28)$$

Hence

$$\frac{D\varpi}{Dt} = \frac{c^2}{\rho} \frac{D\rho}{Dt} = c^2 \nabla^2 \phi. \quad (29)$$

We may eliminate ϖ , so far as it appears explicitly, between (27) and (29). The result is rather long, but in the case of spherical waves it reduces to

$$\frac{\partial^2 \phi}{\partial r^2} + \frac{2}{r} \frac{\partial \phi}{\partial r} = \frac{1}{c^2} \left\{ \frac{\partial^2 \phi}{\partial t^2} - 2 \frac{\partial \phi}{\partial r} \frac{\partial^2 \phi}{\partial r \partial t} + \left(\frac{\partial \phi}{\partial r} \right)^2 \frac{\partial^2 \phi}{\partial r^2} \right\}, \quad (30)$$

as is easily verified. Since c is in general a function of ρ , this equation has to be combined with (28).

Some estimate of the importance of the expression on the right-hand is obtained if we substitute the values of ϕ which were found on the hypothesis of incompressibility, just as if we were attempting a second approximation. Taking, for instance, the formulæ (1) and (16) with $\gamma = \frac{4}{3}$, we get

$$-\frac{2c_0^2}{c^2} \frac{\dot{R}}{r} \left\{ \frac{R_0^3}{R^3} + \frac{R_0^3}{r^3} - 2 \frac{R^6}{r^6} \left(\frac{R_0^3}{R^3} - \frac{R_0^4}{R^4} \right) \right\},$$

Since the same hypothesis makes the terms $\partial^2 \phi / \partial r^2$ and $2\partial \phi / r \partial r$ equal to $\pm 2R^2 \dot{R} / r^3$, it would appear that, provided the ratio c_0^2 / c^2 is small, the second member of (30) is negligible in the neighbourhood of the boundary ($r=R$). The argument is of course far from rigorous, but it is of a kind to which we are often constrained to have recourse in mathematical physics.

At a sufficient distance from the origin the ordinary theory of sound-waves, in which terms of the second order are neglected, becomes applicable. We have then as usual

$$\phi = \frac{1}{r} f\left(t - \frac{r}{c}\right), \quad (31)$$

$$\frac{p-p_1}{\rho} = \frac{\partial \phi}{\partial t} = \frac{1}{r} f'\left(t - \frac{r}{c}\right), \quad (32)$$

$$q = -\frac{\partial \phi}{\partial r} = \frac{1}{r^2} f\left(t - \frac{r}{c}\right) + \frac{1}{cr} f'\left(t - \frac{r}{c}\right), \quad (33)$$

where c is now regarded as constant. As regards the pressure, the only deviation from the case of incompressibility is that changes are propagated, not instantaneously, but with the finite velocity c , with of course the usual attenuation due to increase of distance from the source. The law of transmission of velocity is, however, modified. Except for the "retardation" r/c the first term in the value of q is the same as if the fluid were incompressible, whilst the additional term is equal to $(p-p_1)/\rho c$. The relative importance of the two terms depends on the ratio

$$\tau = f\left(t - \frac{r}{c}\right) \bigg| f'\left(t - \frac{r}{c}\right), \quad . \quad . \quad . \quad (34)$$

which is of the nature of a time. This (variable) time measures the degree of slowness with which the strength of the virtual source $f(t)$ was changing at the instant when it started the waves which in time t have travelled the distance r . Writing (33) in the form

$$q = \frac{p-p_1}{\rho c} \left(\frac{c\tau}{r} + 1 \right), \quad . \quad . \quad . \quad (35)$$

it is seen that the first term preponderates when $c\tau$ is large compared with r , and is relatively insignificant in the opposite extreme. These relations are familiar in the case of a periodic source of sound, where τ may be identified with the period. Sufficiently near the source the motion is practically the same as if the fluid were incompressible. And the range of r to which this statement applies is greater, the lower the frequency.

In the present problem the value of τ is infinitesimal at the front of the advancing wave, where there is an abrupt change of conditions. We have there

$$q = (p-p_1)/\rho c, \quad . \quad . \quad . \quad (36)$$

simply, as is otherwise evident from consideration of the transfer of momentum.

XXIV. *Physical Constants and Ultimate Rational Units.* By
GILBERT N. LEWIS, *Professor of Chemistry, The University
of California* *.

A NEW empirical law usually involves one or more constants, and if the law appears to be general and fundamental these constants are called constants of nature. The discovery of every such constant is indeed a milestone in the progress of science. Nevertheless, to call these quantities natural constants is a characteristically human attempt to shift responsibility. Adopting an old-fashioned phraseology, there is nothing nature abhors more than an arbitrary number which possesses no intrinsic meaning. Perhaps, therefore, it would be better to call them unnatural constants, and reserve the term natural constants for simple numbers like 2 or π .

If we accept the view that is set forth in this paper, and consider that every physical constant indicates some flaw in our scientific system, it becomes as useful a scientific service to eliminate these constants as to discover them. Such an elimination has often been secured by a mere change in the units of measurement; and thus by the two-fold process of discovering new constants and then of reducing these constants to unity or simple numbers, by a change in the system of units, we are progressing toward a more natural or "rational" set of physical units.

The Metric or C.G.S. System.

The units of the metric system are completely arbitrary. Certainly there is nothing fundamental to physics in the period of rotation of the earth, or the dimensions of the earth, or the density of an arbitrarily chosen substance at an arbitrarily chosen temperature and pressure. On the other hand, the introduction of the c.g.s. system represented in two respects a great advance toward the adoption of natural units.

Whether or not it is the best system of counting, the civilized world has definitely adopted decimal numbers; and it was therefore very desirable to replace those systems of weights and measures, inherited from prehistoric civilizations which used other (and possibly better) number systems, by a set of units which stand in simple decimal ratio to one another.

From the standpoint of physics, a far greater advance was

* Communicated by the Author.

secured by the c.g.s. system in fixing the secondary units, such as those of momentum and energy. While the centimetre, gram and second are entirely arbitrary, the ratios between them and the secondary or derived units are made natural ratios and not arbitrary ones which involve a series of meaningless constants. By this one step modern physical equations have been vastly simplified.

The Mechanical Equivalent of Heat.

When it was discovered that a certain amount of work lost in friction always produced the same quantity of heat, a natural constant was thereby discovered, and the custom has not entirely disappeared of putting this number, the so-called mechanical equivalent of heat, into every equation involving mechanical and thermal quantities. But it is one of the signal accomplishments of the theory of energy that heat and work are now regarded as different manifestations of the same fundamental entity, and are therefore expressed in terms of the same unit. Accordingly it is now the custom to write rational thermodynamic equations without this awkward constant.

However, we must not confuse two distinct mental operations which are involved in such a case. The mere fact that two entities are expressed in the same unit does not force us to regard them as identical. Angular velocity has the dimensions of frequency, and indeed, in the case of uniform rotation, a given angular velocity implies a definite frequency of rotation. But the two ideas are distinct, notwithstanding the fact that the two quantities may be expressed in the same units. So a person might dispute the *theory* of energy, that work and heat are the same entity, but no one could fail to recognize the convenience of expressing work and heat in the same *units*.

The Constant of Dulong and Petit, and the Gas Constant.

An important physical constant was the one discovered by Dulong and Petit—namely, the heat capacity per gram atom of a solid element. One of Boltzmann's valuable services to science consisted in showing that the constant of Dulong and Petit is merely the gas constant multiplied by 3.

We now see, moreover, that the existence of the gas constant itself is due to the use of units which are not rationally derived from the c.g.s. system. Thus the constant R is defined as the pressure exerted by 32 grams of oxygen when multiplied by the volume and divided by the absolute temperature. We

now know that 32 grams of oxygen contains $N (=6.06 \times 10^{23})$ molecules, and it is evidently less arbitrary to write

$$PV = n \frac{R}{N} T = nkT,$$

where n represents the number of molecules, and k is called the molecular gas constant.

When PV is expressed in ergs and T is expressed in terms of the Celsius degree, $k = 1.372 \times 10^{-16}$. Now the value of the degree was decided upon without reference to the c.g.s. system, and might as well have been taken of such magnitude as to make the molecular gas constant unity. Complete justification for such a choice is seen in the fact that in the radiation equations of Rayleigh and Planck, which have no direct relation to the properties of gases or of molecules, T is accompanied by the same constant k . A degree which is $1/1.372 \times 10^{-16}$ times as great as the Celsius degree we may therefore call the c.g.s. unit of temperature.

A further consequence of this step deserves comment. The whole theory of the dimensionality of physical quantities has been obscured by the existence of physical constants, to which dimensions are often assigned. Now while it might seem reasonable to assign dimensions to R or k , it would be highly inconvenient to give dimensions to a pure number and especially to unity, which does not even appear in the physical equations. We are thus forced to give c.g.s. temperature the dimensions of energy, and express it in ergs.

Electric and Magnetic Units.

In the development of electromagnetic theory numerous constants might have entered if, for example, the earth had been taken as a unit magnet, or if the unit of charge had been defined as the amount to which some condenser is charged by a Grove cell. On the contrary, every effort was made to choose units which would be rational in the c.g.s. system. Nevertheless, there arose two systems of measurement, the electrostatic and the electromagnetic, and the ratio of the two became a new constant of nature. Later, one of the prodigious successes of Maxwell's theory consisted in the recognition of the identity between this constant and another important constant— c , the velocity of light.

Throughout electromagnetic theory we find numerous equations in which the constant c appears, and always with the time t and to the same power as t . It is evident that the

appearance of this constant is not due to any faulty application of the c.g.s. method, but rather to the arbitrary choice of the primary c.g.s. units themselves.

The Rational Unit of Time.

Especially through the development of the new kinematics of Einstein we are forced to the inevitable conclusion that the most rational choice of temporal and spatial units would be one whereby the velocity of light would be made equal to unity. If provisionally we retain the centimetre as the unit of length, the unit of time must be made 2.999×10^{10} times as small as the second.

Here, again, making the constant unity requires us for convenience to make it dimensionless, and we therefore call the new unit of time the centimetre, and we write $1 \text{ sec.} = 2.999 \times 10^{10} \text{ cm.}$

Once more it is to be pointed out that the use of the same unit for time and for length does not mean that we need regard time and space as completely indistinguishable. Indeed, any one conversant with the 4-dimensional geometry of relativity, while recognizing the great convenience of a common unit, must also recognize that between the concepts of time and space there is a fundamental distinction which relativity does not remove.

Units of Mass, Momentum, and Energy.

A further consequence of relativity is that the energy and the mass of a body vary proportionally to one another, and that the factor of proportionality is the square of the velocity of light. Moreover, if we take velocity as dimensionless, mass and energy have the same dimensions, and therefore we may say that $1 \text{ gm.} = c^2 \text{ ergs.}$ With the new unit of time the rational unit of both energy and momentum is the gram.

The Theory of Ultimate Rational Units.

Starting with the four units of length, time, mass, and temperature, we have seen that by making the molecular gas constant and the velocity of light equal to unity, the number of units may be reduced to two—namely, the centimetre and the gram. It is evident that by using in the same way two other fundamental constants, these two arbitrary units might also be replaced by less arbitrary ones.

Such a system of units was indeed suggested by Planck *, who proposed to make equal to unity, not only k and c , but

* Planck, *Vorlesungen über die Theorie der Wärmestrahlung.*

also h , the constant of the Planck radiation formula, and f , the constant of gravitation. This would give new units for length, time, mass, and temperature "which independently of special bodies or substances would retain their significance for all times and for all civilizations, even those beyond the terrestrial and the human."

While granting the presumptive truth of this statement, the question still remains as to whether the constants chosen in this refixing of the four units are the best ones, and used in the best way. Such a choice would, as far as was apparent, eliminate only four of our physical constants, leaving numerous others which might perhaps equally well have been chosen for the determination of the primary units.

It was at this point that Dr. E. Q. Adams and I advanced our theory of ultimate rational units*. According to this theory there is possible a set of units in terms of which all universal constants (and not merely those which are employed in defining the units) will be reduced to simple numbers. The system of ultimate rational units will be the one in which these numbers are in general the simplest.

In attempting, therefore, to determine the new units of length and mass, we must look for two relations which are as simple and as inevitable as those which we have used to eliminate the arbitrary units of temperature and of time. These two relations will then enable us to replace the gram and the centimetre as well as the units of time and temperature by ultimate rational units.

Hitherto we have been able to decide only upon one such relation, which therefore merely permits us to express all other units in terms of a single one. For this one we shall provisionally retain the centimetre.

The New Unit of Mass or Energy.

It seemed to us that the most fundamental of the outstanding constants was the elementary charge—that is, the charge possessed by an electron or by a univalent positive ion, and we chose the fundamental constant $(4\pi e)^2$, where e is the electron charge in ordinary electrostatic units, namely 4.774×10^{-10} . Now, in ordinary units the square of a charge has the dimensions of energy times length; and if we take new units of mass and energy such that $(4\pi e)^2$ is unity and dimensionless, then the new unit of energy or mass becomes the reciprocal centimetre, and we may write

$$\begin{aligned} 1 \text{ erg} &= 2.779 \times 10^{16} \text{ reciprocal centimetres;} \\ 1 \text{ gram} &= 2.499 \times 10^{37} \text{ reciprocal centimetres.} \end{aligned}$$

* Lewis and Adams, *Phys. Rev.* iii. p. 92 (1914).

Thus energy and mass acquire the dimensions of curvature, or frequency, or acceleration. Indeed, it will be noted that we have now reduced all physical quantities to the dimensions of a power of length. Although this change seems radical, I claim emphatically that we are introducing no new element into the theory of physical dimensions; what we do is no more than has been repeatedly done before in other cases, ever since the introduction of the c.g.s. system.

The Constant of Stefan's Law.

The first success of the theory of ultimate rational units came in the calculation of the constant of Stefan's law. According to this law, if E/V is the energy-density of a hohlraum, $E/V = aT^4$. We concluded that when these quantities were all expressed in terms of ultimate rational units, the constant a would become unity. We were thus able to calculate a value of Stefan's constant, claiming a much higher accuracy than the values which had then been obtained by experiment.

In the two years preceding the publication of our paper, seven determinations of this quantity had been made, as shown in Table I. The results were by no means concordant, the average deviation from the mean being 3.8 per cent. As against the average of 5.81 (for $ac/4$), our calculated value was 5.70, and we predicted that more careful determinations would yield this value. Recently, after a thorough reinvestigation of the subject, Coblentz has obtained the value 5.72 ± 0.012 , in almost perfect accord with the value which we calculated.

TABLE I.

Stefan's Constant (1912-1913).

Author.	$(ac/4) \times 10^5$.
Shakespear	5.67
Gerlach	5.80
Kurlbaum	5.45
Puccianti	5.96
Westphal	5.54
Keene.....	5.89
Fery and Drecq	6.33
Average	5.81
Average deviation 3.8 per cent.	
Calculated (U.R.U.).....	5.70
Coblentz * (1917)	$5.72 \pm .012$

* Coblentz, Proc. Nat. Acad. Sci. iii. p. 504 (1917)

Planck's Constant.

With an accurate value of Stefan's constant, it was possible to obtain therefrom the constant of Planck, assuming the correctness of his radiation formula. In ordinary units the value so calculated was 6.560×10^{-27} . At that time the value obtained in the Bureau of Standards by Coblentz was 6.615, differing from our calculated value by 0.055. Recent determinations, however, have almost completely verified the one which we calculated. Later work by Coblentz* led to the value 6.557, and the mean* of many recent determinations of this quantity is 6.554, differing by only 0.003 and 0.006 from the value we predicted.

Unless, therefore, we are to assume a bizarre coincidence, the recent determinations of the constants of Stefan and Planck furnish a striking justification of the ideas which Dr. Adams and I advanced.

The Entropy of a Monatomic Gas.

In classical thermodynamics the theory of an ideal monatomic gas was given by the expression

$$S = \frac{3}{2}R \ln T + R \ln V + \text{const.},$$

and the constant was regarded as undetermined and undeterminable. With the advent of the third law of thermodynamics, and especially in consequence of the work of Planck, we are now able to assign a definite finite entropy to every substance, and to calculate these entropies from simple measurements.

When this was done it was observed by Sackur† that the numerical values obtained for the entropy of monatomic gases permitted the constant in the above equation to be broken up into two terms, one of which depends only upon the atomic weight, and the other of which is a universal constant which is independent of the nature of the gas. Thus, if W is the atomic weight,

$$S = R \ln (T^{3/2} W^{3/2} V) + C,$$

$$S = R \ln (C' T^{3/2} W^{3/2} V),$$

where $R \ln C' = C$.

Now, if we replace W and V by the mass of one molecule and the volume occupied per molecule, then convert T into c.g.s. units of temperature, and finally reduce everything to

* See Birge, *Phys. Rev.* xiv. p. 361 (1919).

† Sackur, *Ann. Phys.* xxxvi. p. 598 (1911); xl. p. 67 (1913).

our new units, it is a consequence of the theory of ultimate rational units that C and C' must be pure numbers, and probably simple numbers. The only way in which they can both be made simple numbers is to assume that in the new units $C'=1$ and $C=0$. Accepting these values and converting back to ordinary units, we find

$$C' = \frac{k^{3/2} c^3}{N^{5/2} (4\pi e)^6} = 3\,252 \times 10^{-3}.$$

Thus with the aid of a simple deduction from the theory of ultimate rational units, and with no other information whatsoever, we may calculate the entropy of any monatomic gas. Of the several monatomic gases whose entropies have been experimentally determined, there are only four for which the data are at all accurate. The experimental values for these four gases (expressed in calories per degree), together with those calculated from the equation which I have just given, are shown in Table II. The agreement is remarkable, being in every case within the limits of possible experimental error. As in the previous calculation of the constant of Stefan's law, the constants employed in the present calculation are sufficiently well known to give the calculated values an accuracy at least ten times that of any present measured value. Here, again, I venture to predict that new experimental determinations will bring the entropies constantly nearer to those calculated from the equation here given.

TABLE II.

Entropy* of Four Monatomic Gases at 25° C. and 1 atmos.

	Exp.	Calc.
He	29.2	29.8
A	36.4	36.7
Cd	40.0	39.8
Hg	41.3	41.5

The atomic weights of these four gases range from 4 to 200. Moreover, there is evidence † that within the rather wide limits of experimental error the same equation is applicable to the electron with its very much smaller mass. This conclusion has permitted an interesting investigation of stellar spectra in the hands of Saha ‡.

* These values are taken from a paper by Lewis, Gibson, and Latimer, J. Am. Chem. Soc. xlv. p. 1008 (1922).

† See Laue, *Jahrb. Radioakt. Elektronik*. xv. p. 257 (1918). Tolman, J. Am. Chem. Soc. xliii. p. 1592 (1921).

‡ Saha, *Phil. Mag.* xl. p. 72 (1920).

On account of the unfamiliarity of the ideas which we are dealing with, and lest anyone believe that we are here confronted by a mere numerical coincidence such as occasionally appears in scientific calculations, it may be of interest to describe very briefly the manner in which the value of the constant was first obtained. When I became convinced through a paper by Tolman* that Sackur's equation expressed an exact law of nature (except for the values which he, and later Tetrode†, assigned to the constant), I predicted that this constant (C) would be equal to zero in ultimate rational units. At that time I had no idea, except one based on the theory of ultimate rational units, that this prediction would be correct even in order of magnitude. Indeed, when at the first opportunity I carried out the calculation, I found a discrepancy between theory and experiment involving a factor of 10^{20} . At this point some of my colleagues were inclined to doubt the validity of the theory, but feeling confident that some material error must have entered I repeated the calculation, discovered this to be the case, and obtained the very satisfactory agreement with experiment shown in Table II.

Ultimate Rational Units and the Principle of Similitude.

Dr. Adams and I were struck by the fact that not all, but all of the more universal, physical constants with which we had to deal (except the constant of gravitation) had the dimensions of some power of energy times length (or time) in the c.g.s. units, and were therefore dimensionless in ultimate rational units. This is true of the elementary charge, of Stefan's constant, and of the Planck constant, to which we may now add the constant C' of the entropy equation. The idea that this might be a general law has been embodied by Tolman, together with the ordinary theory of dimensionality, in the very interesting theorem which he calls the principle of similitude. This principle is equivalent to a statement that every new fundamental constant will be found to be dimensionless in ultimate rational units.

While we may doubt the complete generality of this principle, it is sure to prove a useful guide to new physical laws.

The Elimination of the Centimetre.

One fundamental constant which is not dimensionless in ultimate rational units is the one discovered by Rydberg. By employing such a constant it is possible to remove the last element of arbitrariness from our system of units. At once

* Tolman, J. Am. Chem. Soc. xlii. p. 1185 (1920).

† Tetrode, *Ann. Phys.* xxxviii. p. 434 (1912).

we might do away with the centimetre, and obtain simplification in our equations, by choosing the mass of the electron as the unit of mass, or h times ν_0 (Rydberg's constant) as the unit of energy. But we shall do well to wait until we can make sure in this step also that the more rational units that we choose are the ones that are likely to prove the best permanently, and may therefore deserve the name of ultimate rational units.

Berkeley, California.

NOTE BY O. J. L.

The publication of a paper does not mean agreement with its contention. I for one hold that an attempt to unify essentially different physical quantities, and obliterate the ratios or constants connecting them, can only result in confusion. *A unit is not unity.* Length and Mass and Time and Energy and Momentum are not the same. Nor is Temperature identical with Energy. Different things sometimes appear to be of the same dimensions, like Work and Moment of force; but there is an element of direction involved even there, and a scalar product differs from a vector product. On the other hand a frequency may rightly be identified with a phase-angle divided by time, which is essentially an angular velocity. So also the identification of Heat and Energy was serviceable, indeed momentous. Any real relation between constants, like $\mu Kc^2=1$ or the expressions of Rydberg and of Planck, is of high value; but the arbitrary elimination of constants, or the attempt to mask them and replace them prematurely by pure numbers, is retrograde.

As to choice of units, that is merely a matter of convenience, not of principle; and a unit of temperature $10^{-16}/1.372$ of a centigrade degree would assuredly not be convenient.

XXV. *The Field of an Electron on Einstein's Theory.*
By S. J. GUNNINGHAM, B.Sc., F.I.A.*

§ 1. *Solution of the Field Equations.*

THE solution of the field equations where the line element is of the form

$$ds^2 = -e^\lambda dr^2 - e^\mu (r^2 d\theta^2 + r^2 \sin^2 \theta d\phi^2) + e^\nu d\tau^2$$

has been given by Nordström † and by Jeffery ‡ for the case $\mu=0$; the field is assumed to be symmetrical in space and static in time.

The solution for the gravitational field of a mass-particle, when $\lambda=\mu$, has been given by Hill and Jeffery §; in this paper it is proposed to give the solution for the field of an electron on this assumption.

The equations of the field, if we suppose matter, apart from the point-mass at the origin, to be absent, are, in the usual notation

$$G_{\mu\nu} = -\frac{8\pi k}{c^4} (E_{\mu\nu} - \frac{1}{2} g_{\mu\nu} E), \quad . \quad . \quad . \quad (1)$$

where k is the constant of gravitation and c the velocity of light.

The values of $G_{\mu\nu}$ that do not vanish are

$$G_{11} = \mu'' + \frac{1}{2}\nu'' + \mu'/r - \frac{1}{4}\mu'\nu' + \frac{1}{4}\nu'^2, \quad . \quad . \quad . \quad (2)$$

$$G_{22} = r\{\frac{1}{2}r\mu'' + \frac{3}{2}\mu' + \frac{1}{2}\nu' + \frac{1}{4}r\mu'^2 + \frac{1}{4}r\mu'\nu'\}, \quad . \quad . \quad (3)$$

$$G_{33} = \sin^2 \theta \cdot G_{22},$$

$$G_{44} = -e^{\nu-\mu} \{\frac{1}{2}\nu'' + \nu'/r + \frac{1}{4}\mu'\nu' + \frac{1}{4}\nu'^2\}, \quad . \quad . \quad . \quad (4)$$

Writing the potential vector of the electromagnetic field as

$$\kappa_\mu \equiv (-F, -G, -H, \phi),$$

we have as the only surviving components of the electromagnetic co-variant tensor $F_{\mu\nu}$, the values

$$F_{14} = -F_{41} = -\kappa_4'.$$

For the corresponding contra-variant tensor, we shall have

$$F^{14} = -F^{41} = g^{11}g^{44}F_{14} = e^{-(\mu+\nu)}\kappa_4'.$$

* Communicated by Prof. G. B. Jeffery, M.A., D.Sc.

† Proc. Ac. Amsterdam, vol. xx. p. 1236 (1918).

‡ Proc. Roy. Soc. A. vol. xcix. (1921).

§ Phil. Mag. vol. xli. p. 823 (May 1921).

The mixed electromagnetic energy tensor defined by

$$E_{\nu}^{\mu} = F_{\nu\alpha} F^{\alpha\mu} + \frac{1}{4} g_{\nu}^{\mu} F^{\sigma\tau} F_{\sigma\tau}$$

will then only survive for the values $\mu=\nu=1$ or 4 , and will be given by

$$E_1^1 = -E_2^2 = -E_3^3 = E_4^4 = \frac{1}{2} e^{-(\mu+\nu)} \kappa_4'^2.$$

The scalar E becomes

$$E = g_{\beta}^{\nu} E_{\nu}^{\beta} = 0, \text{ on summation,}$$

while the co-variant tensor $E_{\mu\nu}$ vanishes except for the values $\mu=\nu$, which are

$$\left. \begin{aligned} E_{11} &= g_{11} E_1^1 = -\frac{1}{2} e^{-\nu} \kappa_4'^2, \\ E_{22} &= g_{22} E_2^2 = \frac{1}{2} r^2 e^{-\nu} \kappa_4'^2, \\ E_{33} &= g_{33} E_3^3 = \frac{1}{2} r^2 \sin^2 \theta e^{-\nu} \kappa_4'^2, \\ E_{44} &= g_{44} E_4^4 = \frac{1}{2} e^{-\mu} \kappa_4'^2. \end{aligned} \right\} \dots (5)$$

From (2), (3), (4), and (5) we have the three equations

$$\mu'' + \frac{1}{2} \nu'' + \mu' / r - \frac{1}{4} \mu' \nu' + \frac{1}{4} \nu'^2 = \frac{4\pi k}{c^4} \kappa_4'^2 e^{-\nu}, \quad (6a)$$

$$\frac{1}{2} \mu'' + \frac{3}{2} \mu' / r + \frac{1}{2} \nu' / r + \frac{1}{4} \mu'^2 + \frac{1}{4} \mu' \nu' = -\frac{4\pi k}{c^4} \kappa_4'^2 e^{-\nu}, \quad (6b)$$

$$\frac{1}{2} \nu'' + \nu' / r + \frac{1}{4} \mu' \nu' + \frac{1}{4} \nu'^2 = \frac{4\pi k}{c^4} \kappa_4'^2 e^{-\nu}, \quad (6c)$$

together with a fourth equation derived from the equations of the electromagnetic field:

$$\frac{\partial}{\partial x_{\alpha}} (\sqrt{-g} F^{\beta\alpha}) = 0$$

or

$$\frac{\partial}{\partial r} (e^{\frac{1}{2}(\mu-\nu)} r^2 \kappa_4') = 0 \dots (6d)$$

for the determination of μ and ν .

Equation (6d) gives

$$\kappa_4' = \frac{\epsilon}{4\pi} \cdot \frac{1}{r^2} e^{\frac{1}{2}(\nu-\mu)},$$

where $\frac{\epsilon}{4\pi}$ is a constant of integration.

From (6 a) and (6 c) we have

$$\mu'' + \mu'/r - \frac{1}{2}\mu'\nu' - \nu'/r = 0. \quad (7)$$

Adding to (6 b) and substituting for κ_4' from above, we have

$$\mu'^2 + 2\mu'/r + \frac{1}{4}\mu'^2 = -\frac{\epsilon^2}{4\pi} \frac{k}{c^4 r^4} e^{-\mu},$$

or writing $\rho = \frac{1}{r}$,

$$\frac{d^2\mu}{d\rho^2} + \frac{1}{4}\left(\frac{d\mu}{d\rho}\right)^2 = -\frac{\epsilon^2}{4\pi} \frac{k}{c^4} e^{-\mu}, \quad (8)$$

The solution of this equation is

$$\left(Ae^{\frac{1}{2}\mu} + \frac{e^2}{\pi} \frac{k}{c^4}\right)^{\frac{1}{2}} = \frac{A}{4}\rho + B,$$

where A and B are the constants of integration.

From considerations at infinity,

$$B = \left(A + \frac{e^2}{\pi} \frac{k}{c^4}\right)^{\frac{1}{2}}.$$

Hence

$$e^{\frac{1}{2}\mu} = 1 + \frac{B}{2r} + \frac{A}{16r^2}$$

or

$$e^{\mu} = (1 + p/r + q/r^2)^2, \quad (9)$$

where

$$p^2 - 4q = \frac{\epsilon^2}{4\pi} \cdot \frac{k}{c^4}.$$

From equations (7) and (6 b), substituting the values obtained for e^{μ} and κ_4' , we have after some reduction

$$\nu' = \frac{2pr^2 + 8qr + 2pq}{(r^2 + pr + q)(r^2 - q)},$$

giving, after integration (the constant of integration being zero),

$$e^{\nu} = \frac{(1 - q/r^2)^2}{(1 + p/r + q/r^2)^2}.$$

It is easily shown that these values for e^{μ} and e^{ν} satisfy equations (6 a), (6 b), and (6 c) identically. Hence the

expression for the line element in this case is

$$ds^2 = -(1 + p/r + q/r^2)^2 (dr^2 + r^2 d\theta^2 + r^2 \sin^2 \theta \cdot d\phi^2) + \left(\frac{1 - q/r^2}{1 + p/r + q/r^2} \right)^2 d\tau^2, \quad (10)$$

where

$$p^2 - 4q = \frac{\epsilon^2}{4\pi} \cdot \frac{k}{c^4}.$$

§ 2. Identification of the Constants.

In order to identify the constants ϵ , p , and q , the equations of motion of a charged particle in the field of the electron will be investigated.

The equations of motion are

$$m' A^\sigma = -\frac{1}{c^2} J^\mu F_{\mu}^\sigma,$$

where J^μ is the current vector

$$\epsilon' \left(\frac{dx_1}{ds}, \frac{dx_2}{ds}, \frac{dx_3}{ds}, \frac{dx_4}{ds} \right),$$

and the acceleration vector

$$A^\sigma = \frac{d^2 x_\sigma}{ds^2} + \{ \alpha \beta, \sigma \} \frac{dx_\alpha}{ds} \cdot \frac{dx_\beta}{ds}.$$

On substitution of the values of the surviving Christoffel symbols, we obtain for the equations of motion

$$\frac{d^2 r}{ds^2} + \frac{1}{2} \mu' \left(\frac{dr}{ds} \right)^2 - (r + \frac{1}{2} r^2 \mu') \left(\frac{d\theta}{ds} \right)^2 - (r + \frac{1}{2} r^2 \mu') \sin^2 \theta \left(\frac{d\phi}{ds} \right)^2 + \frac{1}{2} c^2 \nu' e^{\nu - \mu} \left(\frac{dt}{ds} \right)^2 = \frac{\epsilon \epsilon'}{4\pi} \cdot \frac{1}{m' c^3 r^2} e^{\frac{1}{2}(\nu - 3\mu)} \cdot \frac{dt}{ds}, \quad (11)$$

$$\frac{d^2 \theta}{ds^2} - \sin \theta \cdot \cos \theta \cdot \left(\frac{d\phi}{ds} \right)^2 + 2(1/r + \frac{1}{2} \mu') \frac{dr}{ds} \cdot \frac{d\theta}{ds} = 0, \quad (12)$$

$$\frac{d^2 \phi}{ds^2} + 2(1/r + \frac{1}{2} \mu') \cdot \frac{dr}{ds} \cdot \frac{d\phi}{ds} + 2 \cot \theta \cdot \frac{d\phi}{ds} \cdot \frac{d\theta}{ds} = 0, \quad (13)$$

$$\frac{d^2 t}{ds^2} + \nu' \cdot \frac{dr}{ds} \cdot \frac{dt}{ds} = \frac{\epsilon \epsilon'}{4\pi} \cdot \frac{1}{m' c^3 r^2} e^{-\frac{1}{2}(\mu + \nu)} \cdot \frac{dr}{ds}. \quad (14)$$

In the plane $\theta = \frac{\pi}{2}$, (13) becomes

$$\frac{d^2 \phi}{ds^2} + 2(1/r + \frac{1}{2} \mu') \frac{dr}{ds} \cdot \frac{d\phi}{ds} = 0,$$

giving, on integration,

$$r^2 e^\mu \cdot \frac{d\phi}{ds} = \text{constant.} \quad . \quad . \quad . \quad . \quad (15)$$

From (11) and (14), eliminating $\epsilon\epsilon'$, we have, after reduction and integration,

$$e^\mu \left(\frac{dr}{ds} \right)^2 + r^2 e^\mu \left(\frac{d\phi}{ds} \right)^2 - c^2 e^\nu \left(\frac{dt}{ds} \right)^2 + 1 = 0. \quad . \quad (16)$$

For a particle initially at rest, we have

$$\frac{dr}{ds} = \frac{d\phi}{ds} = 0.$$

Hence

$$\left(\frac{dt}{ds} \right)^2 = \frac{1}{c^2 e^\nu},$$

and from (11),

$$\frac{d^2 r}{ds^2} + \frac{1}{2} c^2 \nu' e^{\nu-\mu} \left(\frac{dt}{ds} \right)^2 = \frac{\epsilon\epsilon'}{4\pi} \frac{1}{m' c r^2} e^{\frac{1}{2}(\nu-3\mu)} \frac{dt}{ds}.$$

From these two last equations, we obtain, neglecting terms with higher negative powers of r than r^{-2} ,

$$m' \frac{d^2 r}{dt^2} = \frac{\epsilon\epsilon'}{4\pi r^2} - \frac{m' p c^2}{r^2},$$

which will be the equation of motion of a particle at great distances from the origin.

We may, then, identify the constant ϵ with the electric charge (in Heaviside units) on the attracting particle, and the constant p with $\frac{km}{c^2}$, where k is the constant of gravitation and m the mass of the attracting particle; for this will give the Newtonian expression for gravitational attraction in the second term on the right-hand side of the equation.

$$q \text{ then becomes } \frac{k}{c^4} \left\{ m^2 k - \frac{\epsilon^2}{4\pi} \right\}.$$

It is easily shown by writing $r=f(r_1)$ in the expression for ds^2 given by Nordström, and solving the differential equation obtained by equating the coefficients of the differentials, that the form for ds^2 obtained in (10) is deduced from that expression by writing

$$f(r_1) = r_1(1+p/r_1+q/r_1^2).$$

XXVI. *On the Anomaly of Strong Electrolytes with special Reference to the Theories of J. C. Ghosh.* By HENRY J. S. SAND, D.Sc., Ph.D., F.I.C.; Sir John Cass Technical Institute, London*.

PART II.

Ghosh's Theory of Electrolytic Conduction.

WE now come to the examination of Ghosh's theory of conduction in solutions. The first assumption we have to consider postulates that certain ions are bound, while others, having sufficient kinetic energy, are capable of conducting electricity, or are free to move past each other in the liquid. Since this freedom to move past each other is independent of the current, we must assume that free ions may occupy any position whatever in the liquid. We have already had occasion to refer to the assumption that the ions have a mean disposition in space conforming to regular patterns, and we pointed out that at best these patterns could only be considered "reference arrangements." To obtain a coherent representation of Ghosh's theory of electrolytic conduction it appears to me necessary to assign the following properties to the arrangements of reference. First, the actual arrangement of ions in the solution at any instant is, so far as conduction of the current is concerned, replaceable by that of the reference arrangement, so that to every ion in the actual solution a position in the reference arrangement corresponds. The kinetic energy of an individual ion in the reference arrangement is not in general the same as that in its actual position in the solution, being in some cases greater in others smaller, according to whether its potential energy in the reference arrangement is smaller or greater than in the actual arrangement. The total kinetic energy of translation is, however, in both cases the same, and its distribution in both cases obeys Maxwell's law. Inasmuch as reference arrangements have axes it must be assumed that these may be placed in any arbitrary direction, *e.g.* in that of the applied electric field. Secondly, positions of ions of the same kind in the reference arrangement are interchangeable so far as conduction of the current is concerned, so that, *e.g.* confining ourselves for the moment to binary electrolytes, the work required to remove any one ion from the reference arrangement while all the others are left fixed, has a definite value independent of the ion chosen. This work can readily be

* Communicated by the Author.

calculated to be equal to $2W/\nu$, if W is the work required to separate all the ions completely and ν is their number. The fundamental assumption made by Ghosh is that only those ions "can escape from the field inside the solution" or are "free" whose kinetic energy is greater than G/ν . It will be remembered that the interpretation given by Ghosh to the quantity we have indicated by G is the same as W applied to an original mol; but that we have been compelled to leave the question open whether this interpretation can be justified or not. It may be pointed out here that W/ν and hence possibly G/ν is the work that would have to be done to remove one ion from the system if we could imagine the operation carried out on successive ions in such a way that the amount of work expended on each was the same. This fundamental assumption is in no way supported by proof, and, as mentioned in the introduction, does not lead to Ghosh's final formula (see Chapman and George, *loc. cit.*).

Inasmuch as the transference of electric current through the solution may be considered to consist essentially in the drifting past each other in the direction of the electric field of oppositely charged ions, all transference in directions at right angles to this being ineffective so far as transmission of the current is concerned, we propose to substitute for Ghosh's assumption just referred to, the one: only those ions are "free" whose kinetic energy arising from the velocity component u in the direction of the electric field is greater than G/ν . Indicating the number of ions into which a molecule dissociates by n , so that $\nu = nN$, the condition we have assumed is expressed by saying that only those ions are "free" for which the kinetic energy arising from the velocity-component u is greater than the value

$$K_u = \frac{G}{nN}. \quad . \quad . \quad . \quad . \quad . \quad (22)$$

Another assumption contained in Ghosh's theory is, that the electric field due to other ions has no influence on the mobility of "free" ions. This assumption is probably approximately correct, for it may reasonably be supposed that hindrances to the motion of "free" ions due to the electric field in certain positions are largely balanced by aids in other positions. We now come to an assumption which is an implied one, and which we propose to abandon. It is to the effect, that the contribution of an ion to conductivity is independent of its velocity or that the "mobility" of all ions of a given substance is the same. Owing to the extreme frequency of the collisions that molecules and ions in a liquid

are subject to, what we have called translatory motion will be akin to vibration. Actual translatory motion in a given direction will be extremely slow and will be the result of the frequency with which molecules or ions are capable of slipping past each other in any given direction. This again will depend on frequency of collision and in particular on the velocity-component in the direction considered. In a similar way an externally impressed electric field will be only operative in slightly increasing the probability of ions slipping past each other in its direction. This effect, however, may be supposed to depend on the frequency of collisions the ion is experiencing, and we may reasonably assume it to be proportional to the velocity-component of the ion in the direction of the electric field.

We now proceed to express these hypotheses mathematically. Confining ourselves in the meantime to the consideration of ν ions of one type, the number having a velocity-component in the direction of the electric field between u and $u + du$ is according to Maxwell's theorem :

$$\nu A e^{-\frac{3u^2}{2\bar{c}^2}} du,$$

where \bar{c} is the root mean square velocity of the type considered and A is a constant of known value. According to the hypothesis just proposed, the contribution to the molecular conductivity made by these is

$$d\lambda = \nu \kappa A u e^{-\frac{3u^2}{2\bar{c}^2}} du,$$

where κ is a constant. The contribution to molecular conductivity of the ions having velocity-components between u and infinity is thus :

$$\lambda = \nu \kappa A \int_u^\infty u e^{-\frac{3u^2}{2\bar{c}^2}} du = \nu \kappa A \frac{\bar{c}^2}{3} e^{-\frac{3u^2}{2\bar{c}^2}};$$

so that making $u=0$, we find for the contribution to molecular conductivity of all the ions of the type considered :

$$\lambda_\infty = \nu \kappa A \frac{\bar{c}^2}{3}.$$

For the ratio $\lambda : \lambda_\infty$ we thus have :

$$\frac{\lambda}{\lambda_\infty} = e^{-\frac{3}{2} \frac{u^2}{\bar{c}^2}}.$$

If m is the mass of each ion, K_u the portion of its kinetic

energy arising from the velocity-component u , and N Avogadro's number, we have :

$$\frac{1}{2}mu^2 = K_u \quad \text{and} \quad \frac{1}{3}Nm\bar{c}^2 = \frac{3}{2}RT.$$

Hence, eliminating u and \bar{c} we find :

$$\frac{\lambda}{\lambda_\infty} = e^{-\frac{K_u N}{RT}}.$$

The same formula will hold for the corresponding ratio of any other type of ion and therefore also for the ratio of the molecular conductivities $\mu : \mu_\infty$ arising from the sum of these ions. Expressing K_u in terms of G according to the hypothesis made (equation (22)) we thus obtain :

$$\frac{\mu}{\mu_\infty} = e^{-\frac{G}{nRT}},$$

which is Ghosh's fundamental formula 2, p. 451, *loc. cit.*

We have thus proved that it is possible by a slight alteration of the hypotheses made by Ghosh, to obtain his formula. Moreover, it appears to me that the alterations are inherently defensible and tend to strengthen the theory. On the other hand, we cannot close our eyes to the fact that the number of assumptions which is explicitly and implicitly contained in the original theory gives to the deductions from it the character only of empirical formulæ. Moreover, I have after extended attempts to deduce the subsidiary hypotheses from the fundamental ones come to the conclusion that the former can at best have only approximate validity. Nevertheless it seems to me that the general idea underlying the theory can be defended. It is this, that the small potential-gradients which can be artificially impressed on a solution will, in the case of ions having small kinetic energy, only slightly distort their orbits without leading to effective conduction of the current. Another way of putting this is to say that the current is in the case of the bound ions employed at first in creating kinetic energy which is subsequently annulled by acting in opposition to the current.

*Theories of complete ionization in a uniform dielectric
and Ohm's law.*

We are thus led to the consideration of what seems to me the most serious objection to theories of a completely ionized solute in a medium of uniform dielectric constant. This is, that it appears on such theories that the current should be

employed at first in creating a polarization in the liquid itself, which would later act in opposition to it, and which would be equivalent to a resistance. Hence, the resistance of an electrolytic solution to rapidly alternating currents should be smaller than to continuous current. No such effect has, however, been observed even at very high frequencies*. In fact, it appears that the conductivity should in the first instant when the current is applied have the same value whether internal electric fields exist or not. For, let us consider a thin layer of finite (say, of unit) surface and thickness dx in the electrolyte, taken perpendicularly to the flow of the current, and let the gradient of potential across the layer everywhere be $\frac{dP}{dx}$. If C is the

concentration of electrolyte in the solution, the total amount in this layer, since it may be considered very large in two dimensions relatively to molecular magnitudes, will correspond to the average composition of the solution, *i. e.* it will be equal to Cdx . The distribution of ions in the layer we may, however, suppose to be governed by Boltzmann's theorem, and there will be more ions of negative than of positive potential energy. The total kinetic energy of ions in positions of low or of negative potential energy is thus, according to familiar reasoning, greater than that of ions in positions of high potential energy; but we may assume the distribution of kinetic energy among ions having a given potential energy to conform to Maxwell's law, independently of what that potential energy is. Hence the total distribution of kinetic energy among ions will be the same as it would be in the absence of attraction between them, and if, as we have assumed, the mobility of an ion is proportional to its velocity, the total average mobility in the first instant when the current is applied should likewise be the same whether the ions are in positions where they attract each other or not.

We may consider the matter from another point of view. We may ascribe to ions in positions of negative or low potential energy a higher concentration than to those of high potential energy, so that when the potential gradient $\frac{dP}{dx}$ is first applied for the small time dt , the amount of electricity crossing any small part df of the surface we are

* See J. J. Dowling and K. M. Preston, *Phil. Mag.* xliii. p. 537 (1922); E. D. Eastman, *J. Amer. Chem. Soc.* xlii. p. 1648 (1920); J. J. Thomson, *Proc. Roy. Soc.* xlv. p. 269 (1889).

considering will be $-kC df \frac{dP}{dx} dt$, where k is a constant, whereas the concentration C varies from point to point. The total amount of electricity crossing unit surface will thus be $(\Sigma C df) \frac{dP}{dx} dt$. The amount of substance contained in the layer of thickness dx and unit surface we have been considering is $\Sigma C df dx$ and is also $C' dx$, C' being the average concentration, so that $\Sigma C df = C'$, and hence the amount of electricity crossing unit surface in the time dt will be $C' \frac{dP}{dx} dt$, independently of the circumstance that the concentration of ions in the layer is not uniform. The theories of Milner, Hertz, and Ghosh dealing with conduction in a completely ionized solution have all aimed at determining the condition in the electrolyte when a permanent state is established, and hence they do not bear upon the effect we have discussed.

Similarly these theories all assume that the distribution of ions in the solution is not affected by the passage of the current, since only on this assumption will conduction obey Ohm's law. Milner nevertheless points out* that the passage of the current will tend to alter the distribution of ions into a random one. Ghosh postulates that his "bound" ions should remain bound, irrespective of the magnitude of the applied potential gradient. In the type of system assumed by Ghosh we should, however, expect a small proportion of bound ions, whose kinetic energy almost suffices to make them free, to become quite free when an external potential gradient was applied. This proportion should vary with the applied potential gradient and should cause a deviation from Ohm's law which should become appreciable for high potential gradients. No such deviation has, however, been observed †.

We are thus led to the conclusion that at every instant in which an ion is "bound," it is bound very much more firmly than would be the case for a completely dissociated electrolyte in a medium of continuous dielectric constant, and that the manner in which it is held must be more analogous to chemical combination. We have, however, already seen that on the assumption of a continuous dielectric constant there are cogent reasons for believing in the practically complete dissociation of electrolytes such as sodium chloride.

* Phil. Mag. xxxv. p. 353 (1918).

† See particularly Taylor and Acree, J. Amer. Chem. Soc. xxxviii. p. 2416 (1916).

We therefore find ourselves compelled to abandon the assumption of a medium of uniform dielectric constant and instead to consider the action of the molecules of solvent as that of discrete particles. A similar position has been reached by Milner proceeding on different lines*, who suggests that the general effect of the action of molecules of solvent as discrete particles "would be to increase the attraction between an ion and the nearest one to it of unlike sign at the expense of the attraction of the more distant ones."

It is doubtful whether the time has yet come for an attempt to give a full theory of conduction in an electrolytic solution, but it may be permissible to point out which considerations, in my opinion, are most likely to lead to a representation agreeing to some extent with experiment. On the basis of present-day theories we must assume the molecules of water and other solvents to contain an equal number of positive and negative charges which, for our present purposes may be considered to be point charges, and it appears to be generally accepted that the molecules of water and other ionizing media have polar properties. By this we mean that charges of one sign are disposed unsymmetrically. The simplest, though by no means adequate, representation of a water molecule will therefore be a simple bipole consisting of one positive and one negative charge rigidly connected like the poles of a magnet. This conception appears to have been introduced into theoretical physics by P. Debye†, who successfully employed it to explain the dielectric properties of the medium. It is obvious that if a medium consisting of such bipoles be placed in an electric field and the bipoles are free to set themselves in it, this would give to the medium the properties of one of very high dielectric constant. However, this is opposed by the rotational energy of the bipoles around axes disposed at right angles to their own axes. Thus, in small electric fields the time during which a bipole is set in the direction of the electric field will be only slightly greater than that during which it is in opposition to it. In very powerful fields, such as those near an ion, the rotation of many of the bipoles will be stopped and converted into vibratory motion around a position of equilibrium, so that we shall have, according to Milner, "surrounding each ion a number of polarized water molecules which tend to form chains linking

* *Phil. Mag.* xxxv. p. 363 (1918).

† *Phys. Zeit.* xiii. p. 97 (1912); *Verh. d. D. Phys. Ges.* xv. p. 777 (1913).

together pairs of temporarily nearest oppositely charged ions." Their action would be to a certain extent "analogous to the action of iron filings in forming chains between two magnetic poles." Following up this idea further we may consider each ion in conjunction with one or more water-molecules to be of the nature of a hydrated or complex ion which as a whole would be capable of rotary or vibratory motion. In contrast to the original ion it may very well have polar properties, so that meeting chains of polarized water-molecules in the liquid it might be stopped in its rotation and then, being only capable of vibration around a position of equilibrium, become "bound" or incapable of transmitting current. It is interesting to note that if we have nN isochronous vibrators, the sum of whose energy is nRT , the fraction having a larger energy than $\frac{G}{nN}$ is $e^{-\frac{G}{nRT}}$, which is Ghosh's formula for the fraction of ions that are free in a solution. It may be said to be probable that a further consideration, particularly of the vibrational and rotational energy of molecules of solvent and of solvated ions, will ultimately lead to a satisfactory theory of the anomaly of strong electrolytes.

Test of Ghosh's conductivity formulæ by experiment.

In testing his formulæ by experimental results Ghosh utilizes in the first instance measurements made on solutions of a concentration of one-tenth to one five-thousandth normal, and later, after the introduction of a viscosity correction, extends his examination to solutions of half normal strength. The formulæ contain the parameter μ_{∞} representing the molecular conductivity at infinite dilution which cannot be derived directly from experiment and to which various investigators have attached different values for given electrolytes. Inasmuch as formulæ proposed by other investigators contain more than one parameter, Ghosh's equations may be said to claim a wider generality than any of these. The values utilized for μ_{∞} by Ghosh are higher than those hitherto proposed. Thus for KCl, Washburn* quotes the following, proposed by other investigators: 127.9 (Müller & Romain), 128.3 (Kraus & Bray), 128.5 (Wegscheider), 130.0 (Kohlrausch, and Noyes & Falk), to which is added 129.64 contributed by Weiland in Washburn's laboratory.

* J. Amer. Chem. Soc. xi. p. 196 (1918).

Ghosh's value, on the other hand, is 132.2. Since a one-parameter formula requires for its test at least two experimental values of which one may be made to agree with the formula, we may follow Ghosh's procedure in the case of an aqueous solution of potassium chloride and make μ_{100} agree with the experimental value 122.5. We then calculate μ values for the following concentrations, $C_1=2 \times 10^{-4}$, $C_2=2 \times 10^{-5}$, $C_3=10^{-5}$, as follows: $\mu_1=129.9$, $\mu_2=131.4$, $\mu_3=131.7$; whereas the experimental values found for these quantities in the very accurate work of Weiland are $\mu_1=129.0$, $\mu_2=129.5$, $\mu_3=129.6$. Even if we allow for the great experimental difficulties involved in determining μ at the high dilutions quoted and for the fact that the values contain corrections for the conductivity of the water which are perhaps not altogether certain, it appears that Ghosh's calculated values at extreme dilutions are somewhat high relatively to μ_{100} . We therefore abandon the attempt to make the formula fit extreme dilutions and shall confine ourselves to concentration-ranges of about 10^{-1} to 10^{-3} normal. The most direct and searching test to apply to formulæ such as those of Ghosh connecting two entirely different branches of physical inquiry, is to determine the same constant independently from numbers taken first from the one and then from the other branch and compare the values obtained. This was the method employed in testing Ghosh's formulæ for i values. We deduce from Ghosh's equation for univalent binary electrolytes:

$$\frac{\log_{10} \mu_2 - \log_{10} \mu_1}{\sqrt[3]{C_1} - \sqrt[3]{C_2}} = K, \quad . \quad . \quad . \quad (23)$$

where μ_1 and μ_2 are molecular conductivities at the two arbitrary concentrations C_1 and C_2 (mols/litre), and the constant K has the value

$$K = \frac{\log_e 10 F^2}{10 \sqrt[3]{4} \epsilon R T \sqrt[3]{N^2}}, \quad . \quad . \quad . \quad (24)$$

all the terms having the significance used above in equation (18).

Making for 18° ,

$$\epsilon = 81, \quad T = 291, \quad N = 6.16 \times 10^{23}, \quad R = 8.32 \times 10^7,$$

we obtain from equation (24): $K = 0.1615$. With this may be compared the values for K calculated from conductivity measurements on a considerable number of univalent binary

electrolytes, according to equation (23). See Table V. It will be seen that the agreement is very good, allowing for the searching nature of the test. The mean value for K derived from Table V. is 0.1698. It is interesting to note that from this value the number 5.7×10^{23} would be calculated for Avogadro's constant.

TABLE V.

Values of constant K calculated from conductivity measurements according to equation (23) for comparison with $K = 0.1615$ following from equation (24).

Salt.	C_1 .	C_2 .	μ_1 .	μ_2 .	K .
KCl	$\begin{cases} 10^{-1} \\ 10^{-1} \end{cases}$	$\begin{cases} 10^{-3} \\ 2 \times 10^{-4} \end{cases}$	$\begin{cases} 112.0 \\ 112.0 \end{cases}$	$\begin{cases} 127.6 \\ 129.1 \end{cases}$	$\begin{cases} 0.1555 \\ 0.1521 \end{cases}$
NaCl	$\begin{cases} 10^{-1} \\ 10^{-1} \end{cases}$	$\begin{cases} 10^{-3} \\ 2 \times 10^{-4} \end{cases}$	$\begin{cases} 92 \\ 92 \end{cases}$	$\begin{cases} 106.5 \\ 107.8 \end{cases}$	$\begin{cases} 0.1746 \\ 0.1697 \end{cases}$
LiCl	10^{-1}	10^{-3}	82.4	96.5	0.1884
CsCl	10^{-1}	10^{-3}	113.6	130.6	0.1663
NH ₄ Cl	10^{-1}	10^{-3}	110.7	127.3	0.1664
KBr	10^{-1}	10^{-3}	114.2	129.4	0.1490
KI	10^{-1}	10^{-3}	113.9	128.2	0.1411
KNO ₃	10^{-1}	10^{-3}	105.0	122.9	0.1877
NaNO ₃	10^{-1}	10^{-3}	87.4	101.8	0.1819
KC ₂ H ₃ O ₂	10^{-1}	10^{-3}	84.0	98.3	0.1875

TABLE VI.

Values of K derived from conductivity measurements in methyl-alcoholic solution for comparison with $K = 0.4121$ (equation (24)) and $K' = 0.568$.

Salt.	C_1 .	C_2 .	μ_1 .	μ_2 .	K .
NaI	$\frac{1}{3.2}$	$\frac{1}{5.12}$	68.8	82.2	0.4068
NaBr	$\frac{1}{3.2}$	$\frac{1}{5.12}$	65.8	82.8	0.5253
NaCl	$\frac{1}{3.2}$	$\frac{1}{5.12}$	69.6	81.8	0.5611
KI	$\frac{1}{3.2}$	$\frac{1}{5.12}$	73.8	91.0	0.4784

For univalent binary electrolytes in methyl-alcoholic solution at 25° , we make $\epsilon = 31$, $T = 298$, and find from equation (24), $K = 0.4121$. Owing to the fact that the attraction for

each other of oppositely charged ions is here 2.613 times as great as in aqueous solution, we should expect the formula for K to be modified in a manner analogous to that proposed by Ghosh for bivalent binary electrolytes. For the latter the attraction of two oppositely charged ions is four times as great as that of two univalent ions under similar circumstances, and Ghosh proposes a distribution of ions which leads to a value of his A and therefore of K , $4\sqrt[3]{4}$ times as great as that for univalent ions. In analogy to this, we should suggest for methyl-alcoholic solutions of univalent ions in which the attraction of two ions for each other is 2.613 times as great as in aqueous solution a value of K , $2.613\sqrt[3]{2.613}$ times as great as it would be in aqueous solution, *i.e.* in the present instance $K'=0.568$. With this value we compare that obtained from a number of conductivity measurements which are assembled in Table VI. Here again the agreement may be said to be good.

For salts like $BaCl_2$ the agreement is not so good. Thus for K the value 0.373 is calculated from Ghosh's formulæ, which may be compared with the values derived from conductivity measurements in Table VII.

TABLE VII.

Values of K for salts like $BaCl_2$ for comparison with the value $K=0.373$.

Salt.	C_1 .	C_2 .	μ_1 .	μ_2 .	K .
$CaCl_2$	10^{-1}	10^{-3}	87.9	111.5	0.2836
$SrCl_2$	10^{-1}	10^{-3}	90.2	114.5	0.2845
$BaCl_2$	10^{-1}	10^{-3}	92.2	116.9	0.2831

It may be asked whether Milner's virial values substituted into Ghosh's conductivity formulæ in place of the latter's G values yield better agreement with experiment. This is not the case. In Table VIII. results for the molecular conductivity of potassium chloride calculated according to both formulæ are given. The calculated conductivity at a concentration of $N/100$, at which Milner's and Ghosh's virial values practically agree (see Table I.) has in both cases been made equal to the experimentally found value, and molecular conductivities at other concentrations are calculated from it.

TABLE VIII.

Molecular conductivities of KCl calculated according to Ghosh's formula, using (1) Ghosh's, (2) Milner's virial values. The values for μ_{100} have been made to agree with the observed values.

Concentration...	10^{-1}	5×10^{-2}	10^{-2}	10^{-3}	2×10^{-4}	2×10^{-5}	10^{-5}	0.
μ { observed ...	112.0	115.9	122.5	127.6	129.0*	129.5*	129.6 *	—
calc. with Ghosh's virial ...	111.7	115.7	122.5	127.9	129.9	131.4	131.7	132.7
calc. with Milner's virial ...	104.1	111.7	122.5	129.2	131.1	—	—	132.7

* Weiland's values.

Summary and Conclusions.

1. On the assumption of a uniform dielectric constant of the solvent medium, the view that solutions of electrolytes such as sodium chloride are practically completely dissociated is well founded.

2. Ghosh's formulæ for osmotic pressure and conductivity of solutions must be considered as empirical formulæ. They cover a wide range, but limits have been indicated in several directions.

3. The statement of Ghosh's subsidiary hypotheses has been corrected so as to make them agree with his mathematical formulæ. Although the theory is on the whole strengthened thereby, the number of stated and implied subsidiary hypotheses is so great that the deductions drawn from them cannot be considered essentially different from empirical formulæ.

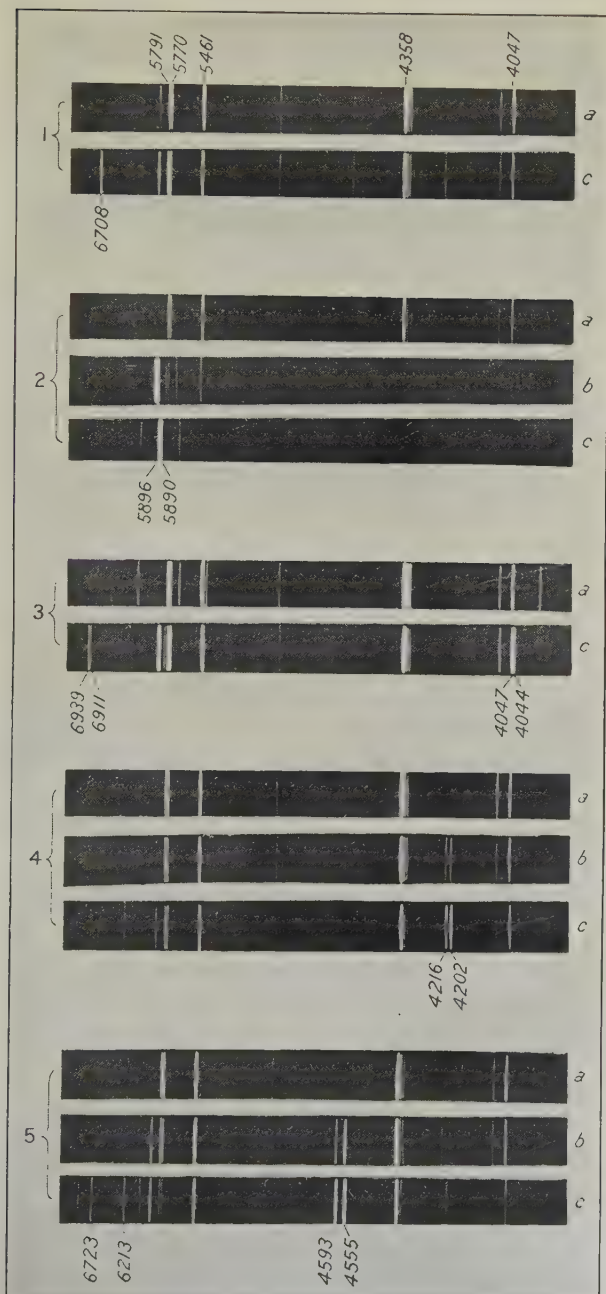
4. Reasons are given to show that hindrances to conduction arising from the electric fields due to ions in a completely dissociated electrolyte dissolved in a medium of uniform dielectric constant would be of the nature of polarization in the liquid itself. Its conductivity should be greater with rapidly alternating currents and under very high potential gradients than with constant small potential gradients.

5. Owing to the absence of such effects as those mentioned under 4, the idea of a solvent medium of continuous dielectric constant has been abandoned, a conclusion previously reached by Milner on different grounds.

6. The nature of the dielectric properties of the solvent as well as its rôle in determining whether an ion is free or bound at a given instant have been considered and the importance of the rotational and vibrational energy of molecules of solvent and solvated ions has been emphasized.

August 1922.

Spectra produced by an Electric Discharge through
a Mixture of Mercury and Alkali Metal vapours.



1. Mercury and Lithium.
2. Mercury and Sodium.
3. Mercury and Potassium

- a. Condensed.
- b. Wehnelt Interrupter.

XXVII. *The Visibility of Individual Spectra.* By F. H. NEWMAN, D.Sc., A.R.C.S., Head of the Physics Department, University College, Exeter*.

[Plate III.]

1. INTRODUCTION.

SPECTROSCOPY furnishes many instances where both the intensity and the nature of the radiations emitted, when an electric discharge is passed through a gas or vapour, depend on the nature of the discharge; argon and the heavier inert gases are the most conspicuous examples. The "red spectrum" of argon is produced by the uncondensed electric discharge, while the condensed discharge develops the "blue spectrum." As the result of mixed conditions a "white spectrum" is sometimes obtained. It is also possible by gradually decreasing the current through the gas to change the colour of the radiation emitted, although the electric force in the tube may remain practically constant. The current density is an important factor in these changes, and it is possible to explain them by considering Bohr's theory of the atom, and the manner in which the atom returns to its normal state after ionization.

The luminosity in an electric discharge-tube does not depend entirely upon the kinetic energy of the moving electrons; for the current, as well as the electric force, affects the brightness, and if the current density is doubled it is found that the intensity of the radiation emitted is more than doubled. The brightness is determined partly by the number of electrons present, for the kinetic energy of the electrons is independent of the current, provided the electric force remains the same.

Although the Lewis-Langmuir theory of atomic structure explains the greatest number of different phenomena, it does not explain the series relation in spectra. The Bohr theory, in conjunction with that put forward by Sommerfeld, of the existence within the atom of a series of non-radiating orbits, any one of which an electron may occupy temporarily, has been found the most satisfactory one; although it accounts for the spectra of hydrogen and helium, it does not explain completely, as yet, the existence of the several series of non-radiating orbits which are necessary to give all the lines of the spectra of elements other than hydrogen and helium.

When an atom is ionized through the inelastic impact of

* Communicated by the Author.

an electron having energy equal to, or greater than, the ionization potential, and recombination takes place, the electron in returning to the orbit which it normally occupies may stop for a short interval at any one of the orbits which are stable, and which are intermediate between the innermost stable orbits and the outside of the atom. As the electron falls from one of these temporary orbits to the next, radiation of that frequency which corresponds to the difference in energy in the two orbits is emitted. Recombination will occur throughout the volume of the gas or vapour, and, as a result, a spectrum consisting of many lines—the number of lines being equal to the number of possible orbits—will be obtained. The question naturally arises whether there is a process during ionization which is the reverse of that occurring during recombination. Does the electron in passing from the atom assume temporarily positions in the stable orbits before it is finally ejected from the atom? If it does, it must proceed by definite steps, and the sum of the energies required for all these steps must equal the ionization potential of the atom. Low voltage arcs in metallic vapours can be explained by this theory. Compton* has suggested that, by the absorption of light, due to the resonance potential, an electron is lifted to one of these stable orbits, and then it requires a smaller amount of kinetic energy from a colliding electron before it is removed completely from the atom. The electron may be raised from the stable orbit to the less stable one by absorption of the corresponding line radiation, or by a colliding electron; and it may be finally ejected from the atom either by absorption of radiant energy, or by the impact of electrons possessing the requisite kinetic energy. Compton states that it is probable ionization is produced at potentials less than the normal ionization potential only in the case of monatomic gases and vapours. This “cumulative ionization” becomes an increasingly important factor in ionization as the ability of any atom to absorb the resonance radiation from neighbouring atoms increases. Then this radiation is passed on from atom to atom, and so the fraction of the atoms which are in the partially ionized state is increased. Complete ionization becomes more general, with the result that the luminosity increases.

The number of atoms in this abnormal state increases as the pressure of the gas becomes greater. The mean free path of the electron is so large at low pressures that it is possible

* Phil. Mag. vol. xliii. (1922).

to develop any required velocity during the interval between successive inelastic impacts. The ionization in this case is due, in the main, to the colliding electrons. When the pressure, and so the number of atoms present, becomes great, with corresponding decrease in the mean free path of the electrons, most of the latter will collide inelastically before the ionization potential energy has been attained, so that the necessary energy must have been acquired partly by the absorption of resonance radiation. At high pressures more radiation will be emitted owing to the greater number of collisions. Increasing the current density will have the same effect.

Considering the discharge of electricity through a mixture of gases or vapours, the relative brightness of the individual spectra is determined by the fraction of atoms ionized. This will depend upon the ionizing potentials, and the actual number of atoms of the components which are present. From what has been stated above, the ionizing potential may be partly acquired by absorption of radiation, so that the current density will be an important factor in the relative luminosity of the spectra, and in the relative brightness of the individual lines in any one spectrum. Argon, for example, has its brightest lines in the less refrangible regions with the uncondensed discharge, while the spectrum developed by the condensed discharge has its brightest lines in the blue. The first line in a principal series is nearly always developed at a lower potential—the resonance potential—than the remaining lines. Owing to the increased energy supplied by the condensed discharge, a greater proportion of the atoms are totally ionized. The electrons in their mean free paths acquire the energy sufficient to ionize the atoms of the gas, with the result that all the lines in the spectrum are developed, whereas with the smaller energy supplied by the uncondensed discharge the electrons only acquire resonance energy and the more refrangible lines in the spectrum are missing. Theoretically, as the energy is increased from the resonance potential to the ionizing potential, successive lines of the spectrum, starting from the less refrangible end, should be emitted. This has actually been observed in the case of mercury vapour by Franck*.

Returning to the case of a mixture of vapours, providing the atoms of the two components are present in equal numbers, that component having the smaller ionizing

* *Zeitschrift für Physik*, xi. (1920).

potential should always emit its spectrum to a greater degree than the other. If, however, the ionizing potential is acquired by "cumulative action" the spectrum will be produced at a potential lower than that normally required, and in this way it is possible for the gas or vapour of the higher ionizing energy to emit the brighter spectrum. Since this effect is greatest at high current densities, such as are obtained with the condensed discharge, if the number of atoms present remain the same, and it is found that the spectrum of the component of greater ionizing potential becomes brighter as the current density is increased, this can be explained by "cumulative action."

In the present work an electric discharge was passed through a mixture of the vapours of an alkali metal and mercury, and keeping the temperature and so the partial pressures constant, the nature of the discharge was varied. It was found that the relative brightness of the individual spectra produced changed considerably as the energy of the discharge was altered.

2. EXPERIMENTS.

A silica vacuum tube fitted with lead seals, and having a capillary portion, was used. The mercury and alkali metal were maintained at 200°C . throughout all the experiments by enclosing the tube within an electric heater. The amounts of the metals present were always such that the partial pressures were the maxima at the temperature employed. The tube was evacuated while the amalgam was kept boiling, in order to eliminate any gaseous impurity such as hydrogen, which is freely emitted from the alkali metals during the first stages of the heating and discharge. The amalgam was made the cathode, and the resulting spectra in the capillary portion of the tube were observed, and were photographed by means of a constant deviation type of spectrometer when an uncondensed electric discharge was passed through the vapours, and also when a condensed discharge was employed. The relative brightness of the spectra changed considerably under these conditions, and some of the results are shown in Plate III. When a Wehnelt interrupter was substituted for the mechanical make-and-break on the coil, the results obtained were intermediate to those given with a mechanical make-and-break, and with a condensed discharge.

The lithium lines were bright when the ordinary discharge was used, although not so bright as the mercury lines. The vapour-pressure of the lithium at 200°C . is exceedingly

small, and it is surprising that the first principal line 6708 is as bright as shown in the photograph. This line and the other lithium lines were completely suppressed when the condensed discharge was employed. With the uncondensed discharge the sodium D-lines always appeared whatever alkali metal was used. They disappeared when the energy of the discharge was increased. The sodium was present as an impurity.

With sodium amalgam, the induction-coil being operated with the ordinary make-and-break, the D-lines were predominant, the mercury lines being almost entirely suppressed. Several of the doublets of the diffuse and sharp series were observed, but they were very weak compared with the D-lines. The latter were very brilliant, and a very bright yellow radiation was emitted from the capillary portion of the tube. At other parts of the tube the mercury spectrum was visible. Replacing the mechanical make-and-break by a Wehnelt interrupter, the mercury lines appeared, although the sodium radiation was still predominant. With the condensed discharge the mercury spectrum became very bright, and hydrogen lines appeared if the discharge was continued for any length of time, the gas being liberated as an impurity from the sodium. The change from the uncondensed to the condensed discharge intensifies the spectrum of the vapour having the greater ionizing potential. It should be noted that the temperature, and so the partial vapour-pressures, remained the same. The alteration in relative brightness of the two spectra is not due to any increase in the number of mercury atoms. At temperatures above and below 200°C . the D-lines were less bright than when the uncondensed discharge was used. It was possible to run the current intermittently for several hours before the characteristic browning of the silica by the sodium vapour made its appearance. The capillary portion of the tube remained quite clear and unobstructed by any condensed sodium vapour.

It has been shown previously by the author* that it is very difficult to excite the potassium spectrum when this vapour is mixed with others. The present experiments seem to indicate that this was due to the excessive current density employed; with a comparatively small current the potassium spectrum was well developed in the presence of mercury vapour, but no lines showed any great brilliancy, and the mercury spectrum was always the brighter. The principal

* *Proc. Phys. Soc.* vol. xxxiii. (1921).

doublet 4044, 4047 was the brightest line of the potassium spectrum, but several of the doublets of the sharp and diffuse series were observed. The lines produced were fainter, under all conditions, than those obtained with the other alkali metal vapours. Potassium has a lower ionization potential than lithium and sodium, so that one would expect its spectrum to be as bright as the spectra of these two elements, especially as its vapour-pressure is greater. The fact that it is not suggests that the "cumulative action" is weak in this case, and any ionization which occurs is produced entirely by colliding electrons. Because of the high vapour-pressure of mercury, few of the colliding electrons attain the ionizing energy, and consequently the luminosity of the spectrum is feeble.

The condensed discharge caused the potassium spectrum to disappear entirely, the mercury lines alone being visible.

The rubidium lines were bright when the ordinary discharge was passed through a mixture of the vapour of this metal and mercury. The principal doublet 4202, 4216 was very prominent. These lines became feeble when the Wehnelt interrupter was used, and disappeared with the condensed discharge, the mercury lines becoming brighter. If the pressure of the rubidium vapour was increased by raising the temperature, the blue doublet became faint compared with the lines in the less refrangible parts of the spectrum, and the radiation in the capillary was pink in colour. At low vapour-pressures the blue doublet became very bright compared with the less refrangible lines, and the radiation was blue in colour. The energy acquired by the electrons between successive inelastic collisions is small at high pressures, with the result that the less refrangible lines are bright. At low vapour-pressures, the mean free path is so large that the ionizing potential energy is attained by the colliding electrons, and the atoms are ionized. The result is the development of all the lines in the spectrum.

The vapour from caesium amalgam gave spectrum results similar to those obtained with the rubidium amalgam. The 4555, 4593 doublet was very bright with the uncondensed discharge, became fainter with Wehnelt interrupter, and disappeared altogether with the condensed discharge, the mercury spectrum completely masking the caesium line. At temperatures below 200° C. the brightest caesium lines were in the blue, and the radiation was pale blue in colour, but at temperatures above 200° C. the colour changed to pink, and the less refrangible lines of the spectrum were brighter than

those in the blue. These effects are similar to those obtained with rubidium.

3. DISCUSSION OF RESULTS.

When the vapours of mercury and any one of the alkali metals are present in a discharge-tube, and the partial pressures are maintained constant, the spectrum of the alkali metal is always well developed with the ordinary discharge, but is completely masked by the mercury spectrum when the condensed discharge is used. All the alkali metal vapours have smaller ionization and resonance potentials than mercury vapour, so that although the amount of the latter present is comparatively great, yet the electrons during their mean free paths between successive inelastic collisions are more likely to acquire the energy necessary for ionization of the alkali metal atoms. As a result, the concentration of the luminous sources may be great enough to exhibit the spectrum of the alkali metal. With the condensed discharge, and consequent increase in the electric energy, a greater proportion of the mercury atoms will be ionized, because the colliding electrons will attain greater energy during their mean free paths. The mercury lines become very bright. At the high pressures used, the mean free path is so small that it is improbable that the ionizing energy can be obtained by impact alone, and it is probably acquired partly by absorption of radiation. That the condensed discharge does cause the electrons to attain more energy during their mean free paths, is shown by the production of the enhanced lines in a spectrum by this type of discharge, for Sommerfeld has shown that enhanced spectra arise from the removal of more than one electron from the normal atom. Under the conditions of the ordinary electric discharge, it is unlikely that an electron in its path will attain sufficient energy for the removal of two electrons. Some of the electrons may be accelerated, without collision, for several mean free paths, far enough to accumulate velocity sufficient to produce the second type of ionization, but the probability of this happening will decrease with rise of pressure. The energy of the colliding electrons does increase with the condensed discharge, and this accounts for the development of the spectrum of those atoms which have the higher ionization potential.

XXVIII. *A Derivation of Planck's Law of Radiation by means of the Adiabatic Hypothesis.* By JAKOB KUNZ, Associate Professor of Physics, University of Illinois*.

WE change the state of a mechanical or electromagnetic system, which is quantified, infinitely slowly by introducing gradually an external field of force or by changing the masses or charges of the particles. A new state of motion will result which is again quantified. This is the adiabatic hypothesis, which has been studied specially by P. Ehrenfest†. Quantities which remain unchanged in adiabatic processes are called adiabatic invariants. It has been shown that such an invariant is the average kinetic energy E_k of a harmonic oscillator divided by the frequency ν . $\frac{\bar{E}_k}{\nu} = \text{constant}$, an equation which holds also for conditionally periodic motions. If the potential energy is proportional to the kinetic energy, we can write

$$\frac{\bar{U}}{\nu} = \text{constant},$$

where \bar{U} is the total average energy of the oscillator. If the temperature radiation is compressed adiabatically in a perfectly reflecting cavity, then we have also for each principal mode of vibration in the cavity:

$$\frac{\bar{U}_s}{\nu_s} = \text{constant}. \quad . \quad . \quad . \quad . \quad . \quad (1)$$

This relation is important in the thermodynamic derivation of Wien's law. Moreover, black radiation remains black radiation by adiabatic compression‡. We shall apply this adiabatic theorem in order to derive Planck's law of radiation in a very simple way.

We shall at first calculate the average energy \bar{U} of molecules or oscillations in an enclosure of constant temperature T . The number of oscillations, dn , whose energy lies in the interval between U and $U + dU$ is by Maxwell-Boltzmann's law given by

$$dn = Ce^{-\frac{U}{kT}} dU. \quad . \quad . \quad . \quad . \quad . \quad (2)$$

* Communicated by the Author.

† P. Ehrenfest, *Ann. der Physik*, li. p. 327 (1916); *Proc. Amsterdam*, xvi. p. 591 (1914). See also A. Sommerfeld, 'Atombau und Spectralinien,' 3rd edit. p. 374 (1922).

‡ Planck, 'Wärmestrahlung,' 2nd edit. Sect. 71.

The total number of oscillations per unit volume shall be N .

$$N = C \int_0^{\infty} e^{-\frac{U}{kT}} dU. \quad . \quad . \quad . \quad (3)$$

Dividing equation (2) by equation (3) we obtain

$$\frac{dn}{N} = \frac{e^{-\frac{U}{kT}} dU}{\int_0^{\infty} e^{-\frac{U}{kT}} dU}. \quad . \quad . \quad . \quad (4)$$

This form of Maxwell-Boltzmann's law we shall modify by the assumption that an oscillator changes its energy not in a continuous way by dU but in an abrupt way by \mathcal{E} , where \mathcal{E} is the quantum of energy. In the cavity we find a number of oscillations each with energy 0, another number with energy \mathcal{E} , another number with energy $2\mathcal{E}$, a number n_s of oscillations each with an energy $s\mathcal{E}$, where s is the quantum number. Equation (4) assumes now the form (5) :

$$\frac{n_s}{N} = \frac{e^{-\frac{s\mathcal{E}}{kT}} \mathcal{E}}{\sum_{s=0}^{\infty} e^{-\frac{s\mathcal{E}}{kT}} \mathcal{E}} = e^{\frac{s\mathcal{E}}{kT}} (1 - e^{-\frac{\mathcal{E}}{kT}}). \quad . \quad . \quad . \quad (5)$$

The energy of these oscillations is equal to $U = n_0 s\mathcal{E}$, and the average energy of an oscillation is equal to

$$\bar{U} = \frac{\sum U}{N} = \sum_{s=0}^{\infty} s\mathcal{E} e^{-\frac{s\mathcal{E}}{kT}} (1 - e^{-\frac{\mathcal{E}}{kT}}), \quad . \quad . \quad . \quad (6)$$

$$\bar{U} = \frac{\mathcal{E}}{e^{\frac{\mathcal{E}}{kT}} - 1}. \quad . \quad . \quad . \quad (7)$$

Now we consider an adiabatic compression of the black body radiation in the enclosure. Before the compression we had :

$$\left(\frac{n_s}{N}\right)_1 = e^{-\frac{s\mathcal{E}}{kT}} (1 - e^{-\frac{\mathcal{E}}{kT}}). \quad . \quad . \quad . \quad (5)$$

Through the compression we change the temperature from T to T' and the energy \mathcal{E} into \mathcal{E}' ; the quantum numbers remain constant. After the compression we have

$$\left(\frac{n_s}{N}\right)_2 = e^{-\frac{s\mathcal{E}'}{kT'}} (1 - e^{-\frac{\mathcal{E}'}{kT'}}).$$

But the character of the relation remains unchanged; hence

$$\left(\frac{n_g}{\bar{N}}\right)_1 = \left(\frac{n_g}{\bar{N}}\right)_2:$$

this equation is satisfied if

$$\frac{\mathcal{E}}{T'} = \frac{\mathcal{E}'}{T}.$$

Before the compression the average energy \bar{U} was given by

$$\bar{U} = \frac{\mathcal{E}}{e^{kT} - 1}. \quad \dots \quad (7)$$

After the compression we have

$$U' = \frac{\mathcal{E}}{\frac{\mathcal{E}'}{e^{kT'} - 1}} = \frac{\mathcal{E}'}{e^{kT} - 1},$$

$$\frac{\bar{U}}{U'} = \frac{\mathcal{E}}{\mathcal{E}'}; \quad \dots \quad (8)$$

but from equation (1) we obtain

$$\frac{\bar{U}}{U'} = \frac{\nu}{\nu'},$$

Hence

$$\frac{\mathcal{E}}{\mathcal{E}'} = \frac{\nu}{\nu'}, \quad \text{or} \quad \mathcal{E} = h\nu, \quad \dots \quad (9)$$

which is the quantum relation of Planck. The average energy \bar{U} becomes now equal to

$$\bar{U} = \frac{h\nu}{e^{kT} - 1}. \quad \dots \quad (10)$$

Rayleigh and Jeans have shown that the number of oscillations do per unit volume in the frequency interval between ν and $\nu + d\nu$ is equal to

$$do = \frac{8\pi\nu^2 d\nu}{c^3}. \quad \dots \quad (11)$$

Hence the energy dE in the same frequency interval is equal to

$$\left. \begin{aligned} dE &= d\omega \bar{U} = \frac{8\pi h\nu^3 d\nu}{c^3(e^{h\nu/kT} - 1)}, \\ \nu &= \frac{c}{\lambda}; \end{aligned} \right\} \dots (12)$$

hence

$$\frac{dE}{d\lambda} = \frac{8\pi hc}{\lambda^5(e^{hc/k\lambda T} - 1)}.$$

This is Planck's law of radiation.

In an oscillation taken at random, we find $f(\nu)$ quanta of energy \mathcal{E} ; therefore

$$dE = \frac{8\pi\nu^2 d\nu}{c^3} h\nu f(\nu). \dots (13)$$

Comparing (13) with (12) we get

$$f(\nu) = \frac{\lambda}{e^{h\nu/kT} - 1}.$$

Laboratory of Physics,
University of Illinois,
October 10, 1922.

XXIX. *Electrolysis with a Dropping Mercury Cathode.*

Part I. Deposition of Alkali and Alkaline Earth Metals.

By JAROSLAV HEYROVSKÝ, D.Sc., Ph.D., Assistant Professor in Physical Chemistry, Charles' University, Prague*.

INTRODUCTION.

B. KUČERA (Drud. Ann. vol. xi. p. 529, 1903) showed that the change of surface-tension of polarized mercury, *i.e.*, the "Electrocapillary parabola," can be very exactly determined by drop-weight. In this method, mercury dropping slowly from a glass capillary in an aqueous solution is polarized, the other electrode being the layer of mercury covering the bottom of the vessel.

In using the dropping mercury as cathode, it has been observed that in neutral or alkaline solutions hydrogen is not evolved even at high polarizations. This arrangement seemed thus convenient to study the cathodic deposition of the most "positive" metals, which are otherwise attacked by water. Besides the high over-voltage the dropping mercury electrode possesses other advantages: it yields in

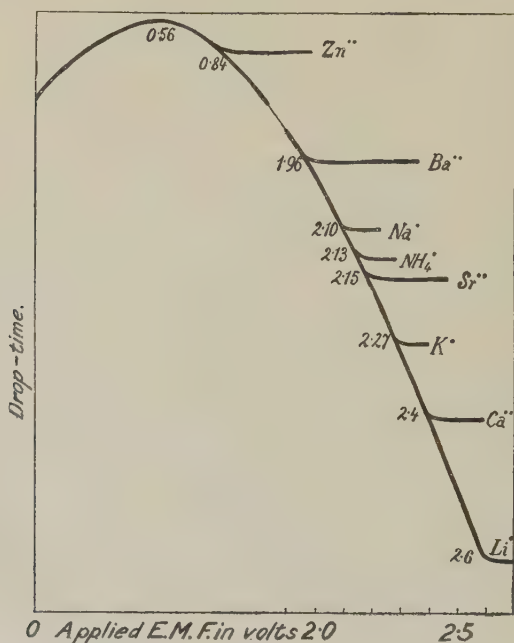
* Communicated by Prof. W. C. McC. Lewis.

the solution always a fresh and pure mercury surface, avoiding thus any "concentration polarization"; further the drops when falling on the bottom mercury used as anode also produce stirring there.

The bottom layer of resting mercury when in a solution of a halide or hydroxide keeps up the well-defined potential of the respective standard electrode, and thus can be relied upon as an exact reference electrode.

With such an arrangement even calcium and magnesium can be deposited in mercury before hydrogen and their amalgam formation can be followed in an exact manner.

Fig. 1.



The ease with which various metals are cathodically deposited in mercury can be determined by observing in each case the shape of the electrocapillary parabola, obtained by the drop-weight method, when readings are continued until considerable amalgam formation is reached. From this point any further increase of polarization does not effect any change in the drop-weight or drop-time. Consequently, when amalgam formation begins, the descending branch of the parabola turns horizontal.

The graph in fig. 1, which refers to decinormal solutions

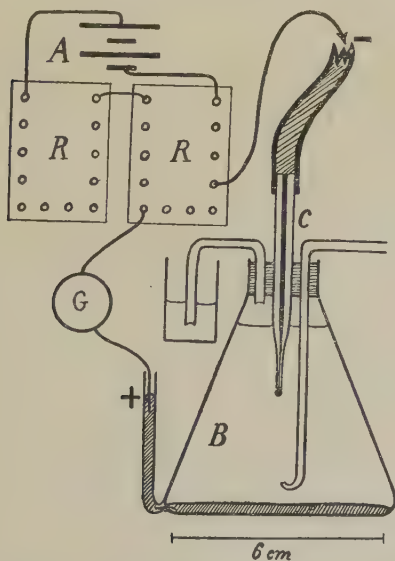
of chlorides of the respective ions, gives us only approximate numbers; the results vary slightly, depending on factors which determine the current, *i.e.*, the size and velocity of drops, strength of the solution, and dimensions of the vessel.

A much more accurate method, however, is to determine in such cases the increase of current caused by the increase of the polarizing E.M.F.; these investigations are described in the following part*.

MEASUREMENT OF THE CURRENT.

The arrangement is shown in fig. 2.

Fig. 2.



The Apparatus. A double lead accumulator A was circuited through two resistance boxes, R. From one of these the current was branched to the electrolysing vessel, which consisted of a conical flask, B, with a platinum contact attached to the bottom; a thick-walled glass capillary passed through the cork stopper C, connected by a rubber tube to a

* See also J. Heyrovský, *Chemické Listy*, vol. xvi. p. 256 (1922).
Phil. Mag. S. 6. Vol. 45. No. 266. Feb. 1923. X

mercury reservoir (not shown in the sketch), by the level of which the rate of dropping could be regulated. The glass tubes, which passed through the stopper, served to lead the hydrogen in and out. The negative terminal of the resistance-box was connected to the mercury reservoir above the capillary, the other was connected through a sensitive galvanometer to the bottom mercury layer in the flask.

The capillaries were drawn out of a thick-walled thermometer capillary, with about 1 mm. inner diameter; they were broken off under water when connected with the mercury reservoir, so that the pure and dry mercury rushed into the tip first. It is essential to have the inside of the tube quite free from dust—however, the capillaries must not be washed nor moistened; for this reason capillaries made of fresh glass have to be used. The break of the tip was chosen so as to yield drops of about 4 to 6 seconds time (*i. e.*, 0.02–0.05 mm. inner diameter of the opening).

Since on prolonged use the capillaries get stopped and moistened inside, which might lead to hydrogen evolution in the tip, they have to be frequently exchanged for new ones.

The reflecting galvanometer of the Kelvin type with an astatic needle had 50 ohms resistance; one millimetre deflexion of scale, when two metres apart from the mirror, corresponded to 10^{-8} ampere.

The Method of Procedure. Before starting polarization, the resistances of the boxes were adjusted so as to be one ohm per millivolt of the E.M.F. of the source (about 4 volts); this E.M.F. was determined by compensation with a standard Weston cell with an accuracy to a tenth of a millivolt and was frequently checked. The vessel was then filled with a solution prepared from Kahlbaum's or Merck's purest specimens, and the stopper was sealed with paraffin-wax. In order to prevent oxidation by air at the cathode, it has been found necessary to pass hydrogen for 30 to 40 minutes through the solution.

The room temperature was kept as close as possible to 20° C.; the maximal deviation $\pm 1^\circ$ had no noticeable effect, which probably lies within the experimental errors of the method.

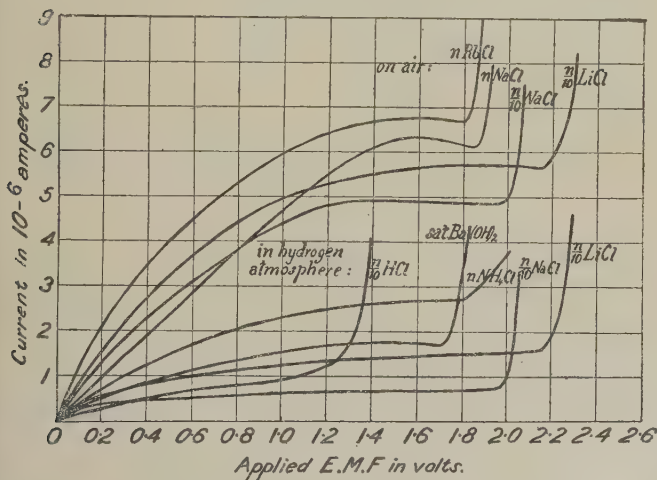
The zero reading of the galvanometer was then taken and the polarization was gradually increased, and for each value of the applied E.M.F. the corresponding galvanometer reading was noted.

OBSERVATIONS.

Some of the typical curves, showing the relation between E.M.F. of polarization and the resulting current, are drawn on the diagram (fig. 3).

When working with solutions in an open beaker in air a small current passes even at small polarizations, which is largely due to oxygen dissolved in solution. The readings in such cases were not steady, but oscillated within sharp limits (1-2 scale divisions) synchronously with the drop-time, this being no doubt caused by the different rates of oxidation of the rhythmically changeable drop-surface. By

Fig. 3.



expelling air with hydrogen, the current was considerably diminished and oscillation stopped entirely.

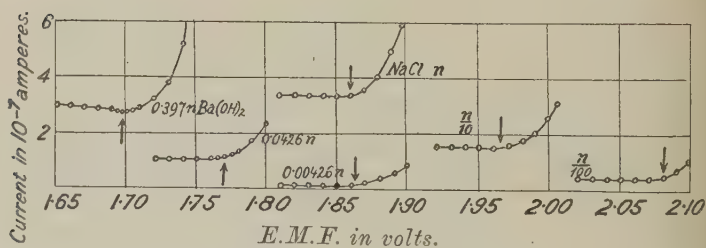
With increasing polarization the current increases at first very slowly until a certain value of the E.M.F. is applied, above which the current increases rapidly, so that a further increase of a few centivolts puts the mirror off the scale. This critical E.M.F. is quite independent of the dimensions of the electrodes of the drop-time and of the amount of air in solution--in fact, it is found to depend only on concentration of the cation.

The independence of the critical polarization, which might be termed the "decomposition E.M.F.," since at this point

extensive electrolysis of the salt sets in, has been ascertained in a series of solutions using different capillaries, with different drop-times (from 1 to 5 secs.), with varying distances between the electrodes (0.5 to 6 cms.) and varying size of bottom layer (from 9 to 60 cm.²), further, with varying external resistance in the boxes (from 0.1 to 10 ohms per millivolt). For very quick drops (less than one sec.) a slight shift towards greater polarizations can be observed; for drop-times greater than 1.5 sec. the results coincided. The slower the dropping, the more steady the galvanometer was; therefore, very narrow capillary openings were used, giving about 3 secs. drop-time at the decomposition polarization.

The decomposition E.M.F. was fixed as the value from which the current begins to increase distinctly in a geometrical progression. Owing to this steep increase it was possible to fix this point in most of the solutions within 2–4 millivolts, in some cases even to a greater accuracy. For this purpose the E.M.F. near this value was increased by 5 millivolts and the exact point found from a graph.

Fig. 4.



The more dilute solutions require larger decomposition E.M.F. (see fig. 4), the differences for a ten-fold dilution of a uni-univalent salt amounting to 110 millivolts, for a bi-univalent salt it is about 80 millivolts, which is the well-known difference of "free energies" at these dilutions (*cf.* McInnes and Parker, Journ. Amer. Chem. Soc. 37, p. 1445, 1915). Solutions prepared (by weight or dilution) at different times and from different sources always led to the same decomposition E.M.F.

Traces of noble metals or oxidizing matter in solution cause disturbances in readings; these become troublesome in very concentrated solutions, which therefore had to be

prepared in a high degree of purity to give satisfactory results. For much help in this way the author is obliged to Professor B. Brauner, who presented some of his rare specimens and provided for exact standard solutions.

When a cathode of very small dimensions is polarized, the large reference electrode being used as anode, the decomposition E.M.F. must be equal to the difference between the potential of the electrode used as anode and the potential at which decomposition takes place at the cathode. Let us denote the latter as the "deposition potential" of the cation in mercury. To show that this deposition potential is independent of the anion, solutions of chlorides and hydroxides of the same metal in various dilutions were electrolysed, and from the results the deposition potentials referred to the normal calomel electrode were calculated. For this purpose the exact potential difference of the bottom reference electrode in the vessel from that of the normal calomel electrode had to be determined. Therefore, for most of the solutions a calomel or mercuric-oxide-electrode has been set up and compared with the standard calomel electrode. The potential of these single electrodes never differed by more than two millivolts from the polarized bottom mercury layer when both were in the same solution.

To eliminate the liquid junction potential between the normal electrode and the various solutions, a quarter-saturated, half-saturated, and fully saturated potassium chloride solution has been used and the values extrapolated.

The results are given in Tables I. and II.

The results show distinctly that the polarization at which electrolysis starts, E , depends only on the concentration of the cation being equal to the difference of potential of the resting mercury and the deposition potential of the cation ($\pi_0 - \pi'$).

The value π_N , which is the deposition potential of the cation from a solution containing one gram-ion per litre, has been obtained from π' actually observed at different dilutions by subtracting the free energy of dilution of the ions; here the average numbers observed in concentration cells at room-temperature were used, viz. :—

For ten-fold dilution of uni-valent cations 0.056 volt.

For 100-fold dilution 0.114 volt (known from silver- or hydrogen-ion concentration electrodes).

For bivalent 0.026 and 0.054 volt respectively (from Zn^{++} , Hg^{++} , Ba^{++} concentration cells).

TABLE I.

Deposition of the Alkali Metals, $t = 20^{\circ} \text{C}$.

Solution.	E the observed decomposition E.M.F.	π_0 observed P.D. of the bottom layer from N. cal.	$\pi' = \pi_0 - E$ the deposition potential of the cation.	π_N the calculated normal deposition potential.
n LiCl	2.05	*0.00	-2.05	-2.05
$\frac{n}{10}$ "	2.16	+0.052	-2.11	-2.05
$\frac{n}{20}$ "	2.22	+0.068	-2.15	-2.07
0.0382 n "	2.26	+0.085	-2.17	-2.07
1.122 n LiOH ...	1.867	-0.1552	-2.022	-2.025
0.108 n "	1.960	-0.1138	-2.074	-2.021
n NaCl	1.860	+0.0010	-1.860	-1.860
$\frac{n}{10}$ "	1.968	+0.0521	-1.916	-1.860
$\frac{n}{100}$ "	2.080	+0.1072	-1.973	-1.859
1.076 NaOH	1.700	-0.1598	-1.860	-1.862
$\frac{n}{10}$ "	1.810	*-0.104	-1.914	-1.858
$\frac{n}{100}$ "	1.925	*-0.048	-1.973	-1.859
n KCl	1.883	0.000	-1.883	-1.883
$\frac{n}{10}$ "	1.990	0.0532	-1.937	-1.881
$\frac{n}{100}$ "	2.108	0.1080	-2.000	-1.886
n RbCl	1.795	*0.0	-1.795	-1.795
$\frac{n}{10}$ "	1.905	*0.053	-1.852	-1.796
$\frac{n}{100}$ "	2.020	*0.108	-1.912	-1.798
$\frac{n}{10}$ CsCl	1.948	*0.053	-1.895	-1.839
$\frac{n}{100}$ "	2.055	0.1077	-1.947	-1.833
n NH_4Cl	1.795	+0.004	-1.791	-1.787
$\frac{n}{10}$ "	1.900	+0.056	-1.844	-1.788
$\frac{n}{100}$ "	2.010	+0.110	-1.900	-1.786

* Values not actually observed, but taken from analogous cases.

TABLE II.

Deposition of the Alkaline-earth Metals, $t=20^{\circ}\text{C}$.

Solution.	E observed.	π_0 observed.	$\pi'=\pi_0-E$.	π_N calculated.
$m\text{MgCl}_2$	1.890	*-0.011	-1.901	-1.901
$\frac{m}{10}$ "	1.970	*+0.039	-1.931	-1.905
$\frac{m}{10}\text{CaCl}_2$	2.090	*+0.039	-2.051	-2.025
$\frac{m}{100}$ "	2.170	*+0.095	-2.075	-2.021
$0.0455n\text{Ca(OH)}_2$	1.985	-0.0880	-2.073	-2.024
$m\text{SrCl}_2$	1.850	*-0.011	-1.861	-1.861
$\frac{m}{10}$ "	1.930	*+0.039	-1.891	-1.865
$\frac{m}{100}$ "	2.010	*+0.095	-1.915	-1.861
$0.119n\text{Sr(OH)}_2$	1.782	-0.1140	-1.896	-1.862
$0.0120n$ "	1.857	-0.0627	-1.920	-1.860
$m\text{BaCl}_2$	1.800	-0.011	-1.811	-1.811
n "	1.828	+0.004	-1.824	-1.816
$\frac{n}{10}$ "	1.911	+0.0567	-1.854	-1.822
$\frac{n}{100}$ "	1.981	+0.1088	-1.872	-1.810
$0.397n\text{Ba(OH)}_2$	1.699	-0.1337	-1.833	-1.815
$0.0426n$ "	1.770	-0.0875	-1.858	-1.813
$0.00426n$ "	1.862	-0.0363	-1.898	-1.826

The series of the deposition potentials runs as follows :—

Li	-2.023 volts.	NH_4	-1.787 volts.
K	-1.883 "	Ca	-2.023 "
Na	-1.860 "	Mg	-1.903 "
Cs	-1.837 "	Sr	-1.862 "
Rb	-1.796 "	Ba	-1.814 "

Salts of lithium and calcium, owing to their high cathodic deposition, offered difficulties, since traces of other alkalis or alkaline earths present as impurities are deposited first. Moreover, at such great polarizations in quickly dropping capillaries, especially when long in use, bubbles of hydrogen

are evolved. This was still worse with beryllium salt solutions, which, owing to hydrolysis, did not lead to any satisfactory result. Traces of acidity change the electrolysis of salts to that of hydrochloric acid (see in fig. 3) and then hydrogen is evolved before the metal is deposited.

On the other hand, traces of alkalies stabilise greatly the over-voltage and thus remove fluctuations in readings; the alkalinity, however, changes the potential of the resting mercury, making it more negative, and this change has to be measured and taken into account.

The most suitable for these measurements of polarization are alkaline solutions of hydroxides, not only on account of the scarcity of hydrogen ions, but also that the product formed at the anode is mercuric oxide, which is at the same time the depolarizer used in this electrode. Of all solutions, those of baryta are most favourable, as in this instance the traces of all other positive metals would be deposited at much more negative potentials, and impurities of nobler metals are excluded owing to the alkalinity of the solutions.

Electrolysis of dilute ammonium chloride offered no difficulties; it differs from the deposition of metals in that the current curve does not increase so steeply with increasing polarization (see fig. 3). The same was observed with magnesium salts and in concentrated solutions of calcium, strontium, and lithium.

In dilutions greater than hundredth normal the readings became indistinct, in very concentrated solutions impurities mattered much; in concentrated chlorides, moreover, the formation of complexes with mercury brings it in solution, which causes great increase and oscillations of the current. For a similar reason sulphates cannot be used, since mercurous sulphate is considerably soluble and the solution shows increasing conductance during polarization.

DISCUSSION OF THE RESULTS.

There is no doubt that the sudden change in slope of the current-E.M.F. curve (figs. 3 and 4) is due to amalgam formation at the cathode. The formation of amalgams from electrolysis of salts was studied by Coehn and Kettembeil (1901-4), who used aqueous solutions of calcium, strontium, and barium with a mercury cup as cathode. With such an arrangement, however, extensive hydrogen evolution, besides concentration polarization, excludes satisfactory results. Experiments with resting mercury used as cathode repeated by the present author gave the break at much lower and

very changeable potentials, due only to the evolution of hydrogen, which depends on catalytically acting impurities present in solution.

According to the theory of electrolysis, even the slightest polarization, say 0.1 volt, deposits some cations on to the surface of the mercury drop, and forms there an extremely dilute amalgam. A very minute current equivalent to this deposition must pass through the solution, but, since the drop-surface possesses now a more negative potential, the current is stopped by the opposing E.M.F. In increasing the polarizing E.M.F. we increase the minute amalgam concentration in the drop surface and diffusion into the inside must result. The amount which diffuses will be proportional to the concentration of the amalgam in the surface, which is given by the formula

$$\pi = - \frac{RT}{nF} \log K_{Me} \cdot C_{Me},$$

where C_{Me} denotes the amalgam concentration and π the potential of the polarized drop. Thus the current

$$i = k \cdot C_{Me} = K \cdot e^{-\frac{\pi nF}{RT}};$$

i. e. the curve should be an exponential.

It will be noted that the increase of current above the decomposition potential proceeds in a geometrical progression, the curve resembling a steep exponential.

The concentration of the amalgam in the drop-surface at the deposition potential can be estimated from the investigations of G. N. Lewis and his co-workers (1912-15) on the alkali-metal amalgam potentials. Assuming that ten-fold dilution of the extremely dilute amalgam lowers its potential by 0.06 volt, we obtain from the available data a concentration of the order 10^{-6} gram atoms of alkali metals per litre of mercury. *i. e.*, about one millionth of one per cent.

Mercury Drop Potentials. An attempt was made to measure the potential of polarized mercury by placing under the dropping capillary in the electrolysing flask B (fig. 2) a glass cup with a platinum contact. Normal and tenth-normal sodium chloride solutions were used; the potential of the drops collected in the cup was measured against the bottom mercury, or, which was found always to be identical, against a normal or deci-normal calomel electrode connected with the solution. From the beginning of the polarization

and also at the decomposition E.M.F. the drops showed no difference against the pure resting bottom mercury; however, 40 to 60 millivolts above the decomposition potential the drops in the cup showed already 2 millivolts difference from pure mercury, and this difference increased rapidly, so that at a polarization of 2.10 volts the mercury in the cup was already negative by nearly 2 volts more than the reference electrode. Obviously the most dilute amalgams which are formed at the deposition potential are only superficially polarized and lose their negative potential during the fall, being instantly acted upon by water.

Affinity for Mercury. It is assumed that the positive metals combine with mercury and their compounds are rich in mercury. Recently Richards and Conant (J. Amer. Chem. Soc. xlv. (1922) p. 601) pointed out that even at very great dilutions amalgams do not behave as ideal solutions, showing a rather large decrease in potential and a considerable heat of dilution. The explanation is that even at such dilutions combination with mercury still proceeds.

Supposing complete saturation will once be reached, in an enormously dilute amalgam, as is probably the case in the surface of slightly polarized mercury, we cannot expect that this enormously dilute amalgam will have a tendency to diffuse inside the drop as the particles are lighter than mercury and are completely "solvated" with mercury. As soon as the the amalgam concentration increases so far that it will not allow all atoms to be fully solvated with mercury, affinity for mercury as well as the increased concentration will cause diffusion into the interior of the drops; from this point the current curve will proceed much steeper than ordinary diffusion could effect, and this probably happens at the deposition potential.

The atoms of the alkali metals in the surface of mercury are under two opposing forces; the affinity for mercury draws them into the surface, their solution tension, on the other hand, sends them into solution. Thus the deposition potential depends both on the affinity of the metal for mercury and its electrolytic potential. Since at the deposition potential all alkali metals are in an analogous condition, we can use these values to express the relative affinities of the alkali metals for mercury. The deposition potential indicates thermodynamically the very small partial pressure the alkali metal has in the drop-surface; the combination with mercury has lowered the activity of the alkali metal, indicated by its electrolytic potential (E.P.) to the characteristic value π_N .

Thus the affinity, A , of the metal for mercury is equal to $\pi_N - E.P.$

From the work of G. N. Lewis, mentioned above, and the values π_N we have:—

Metal.	E.P.	π_N .	$A = \pi_N - E.P.$
Li.....	-3.304	-2.023	1.281
Na	-2.998	-1.860	1.138
K.....	-3.208	-1.883	1.325
Rb	-3.205	-1.796	1.409
Cs	(-3.3)	-1.837	(1.5)

The affinity is expressed in volt-faradays per gram-atom. This series shows that the affinity for mercury increases with increasing atomic weight. Sodium has an anomalous position (*cf.* McPhail Smith, *Zeitsch. Anorg. Chem.* lviii. (1908) p. 381) and behaves like a nobler metal, its amalgam being very stable—in fact, hydrogen was never observed in these experiments to be formed on mercury drops on electrolysis of sodium solutions. Finally, it may be pointed out that the affinity of caesium for mercury, which from extrapolation would amount to 1.5 volt, points to the E.P. of caesium being -3.3 volt (from the calomel electrode).

Besides to Prof. Brauner, the author's thanks are also due to Professors J. Štěrba-Böhm and F. Závíska for their help.

The author wishes to express his indebtedness to the prematurely deceased Professor B. Kučera, who suggested to him the study of the polarization of dropping mercury.

Chemical Laboratory of
the Charles' University,
Prague.

XXX. Indian Drums.

To the Editors of the Philosophical Magazine.

GENTLEMEN,—

IN India, like kettledrums, there are many drums which are musical, and which are used in company with stringed instruments. They differ from kettledrums in two respects: (1) they are loaded over a central zone, and (2) they elicit harmonic partials ('Nature,' Jan. 15, 1920, p. 500). It is well known that the partials of an unloaded membrane do not form an harmonic series, and a few of them give a consonant chord. From a look at the Indian instruments, it at once becomes evident that the load per unit area varies as

we proceed outwards from the centre. The investigation of the nature of vibration when the load varies inversely (1) as the first power and (2) as the second power of the distance from the centre, can be very simply effected, but the writer could not find any mention in the text-books.

The equation of motion is given by

$$\rho \frac{d^2 w}{dt^2} = T_1 \left\{ \frac{d^2 w}{dr^2} + \frac{1}{r} \frac{dw}{dr} + \frac{1}{r^2} \frac{d^2 w}{d\theta^2} \right\}.$$

Assume $w \propto \cos ket$:

$$\text{Case (1)} \quad \rho = \frac{\rho_0}{r} \quad \text{and} \quad \frac{T_1}{\rho_0} = c^2, \quad . \quad . \quad . \quad . \quad . \quad (1)$$

and further assume $w = v \cos n\theta$, then v must satisfy

$$\frac{d^2 v}{dr^2} + \frac{1}{r} \frac{dv}{dr} + \left(\frac{K^2}{r} - \frac{n^2}{r^2} \right) v = 0. \quad . \quad . \quad . \quad (2)$$

Put $x = 2K \sqrt{r}$, then (2) becomes

$$\frac{d^2 v}{dx^2} + \frac{1}{x} \frac{dv}{dx} + \left(1 - \frac{(2n)^2}{x^2} \right) v = 0; \quad . \quad . \quad . \quad (3)$$

$$\therefore \quad v = A J_{2n}(x) = A J_{2n}(2K \sqrt{r}).$$

If at $r = a$ the membrane is fixed, we must have

$$J_{2n}(2K \sqrt{a}) = 0,$$

giving real values of K . The nature of these roots is well known; they do not form an harmonic series. The effect of the variable density is mainly upon the absolute pitch of the membrane.

$$\text{Case (2)} \quad \rho = \rho_0 / r^2. \quad . \quad . \quad . \quad . \quad . \quad (4)$$

Let us consider the simple case of symmetrical vibrations only, so that (2) becomes

$$\frac{d^2 v}{dr^2} + \frac{1}{r} \frac{dv}{dr} + \frac{K^2 v}{r^2} = 0; \quad . \quad . \quad . \quad . \quad (5)$$

$$\therefore \quad v = B \cos (K \log r). \quad . \quad . \quad . \quad . \quad (6)$$

The boundary condition gives $\cos (K \log a) = 0$;

$$\therefore \quad K \log a = (2n+1) \frac{\pi}{2}.$$

The partials now form a series of odd harmonics, and the absolute pitch is also disturbed.

R. N. GHOSH.

Muir Central College,
Allahabad, India,
3rd Jan., 1922.

XXXI. *Magnetic Valency and the Radiation Hypothesis.*By F. T. PEIRCE, *B.Sc., A.Inst.P.**

MUCH criticism and fresh experimental data have necessitated large modifications on the original simple views of the radiation hypothesis of chemical reaction, such as those advanced by Perrin in his very comprehensive treatment (*Ann. de Phys.* 9, xi. pp. 1-108). The broad synthesis which it gives seems to inhere in some principle of atomic structure, not necessarily dependent upon radiation.

Some serious objections may be avoided and fertile modifications suggested if we inquire into the possible mechanism which might give a peculiarly effective rôle to radiation of definite frequency. This could hardly be expected of a general electrostatic attraction between atoms. There seems no reason why the forces of a collision should not be as efficacious, or more so, in breaking such a bond, nor why the "activation" of a molecule by a change in an electronic orbit should be necessary for its formation.

The frequencies involved in most reactions are much higher than those of the atoms as a whole, and the supposition of their unique rôle is probable only for a local bond between individual electrons. Such an arrangement, suggested by magnetic phenomena, has been pictured by A. E. Oxley (*Proc. Roy. Soc. A* 98, p. 264, 1921) and is shown diagrammatically in fig. 1. This view of the valency bond is very successful in stereo-chemistry and gives more precise physical meaning to the ideas of Langmuir on stoicheometry.

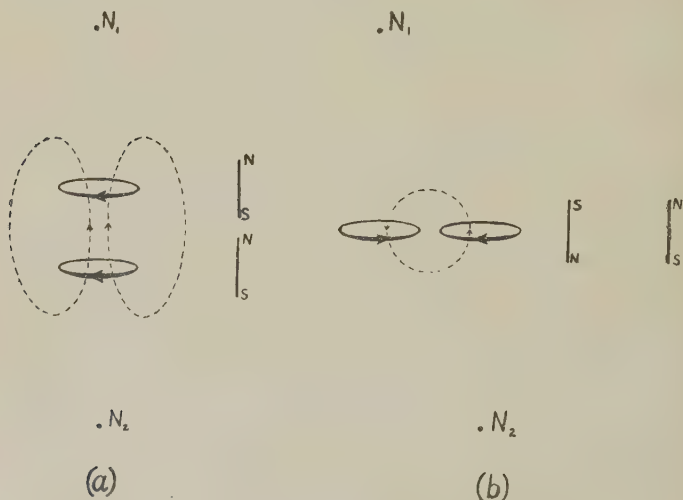
The valency bond is due to the attraction between two elementary magnets, electrons in small orbits, ring or vortical electrons. Either or both of the arrangements of fig. 1 may conceivably exist, their relative stability depending on the unknown dynamical conditions at such minute distances. The doublet in fig. 1 (*a*) is paramagnetic, in fig. 1 (*b*) diamagnetic. They exist where, in Langmuir's theory of chemical combination, electrons are "held in common." The combination of charged ions must be considered separately.

The condition that the electrostatic repulsion should vanish or be greatly exceeded by the magnetic attraction, demands

* Communicated by the Author. Substance read before the Manchester Literary and Philosophical Society, Nov. 29, 1921.

an oscillatory law of force at small distances. This postulate, apparently necessary to the continued existence of matter, has been advanced under several forms, *e.g.*, J. J. Thomson (Phil. Mag. vi. p. 220). The present hypothesis may be extended to atomic phenomena, from which a suitable law might be deduced. For the moment it is sufficient to postulate that, as two such magnetons approach, a point is reached where the electrostatic repulsion is counter-balanced by the magnetic attraction, at some distance small in comparison with infra-red wave-lengths, and depending upon the external field by which the positions of the electrons

Fig. 1.



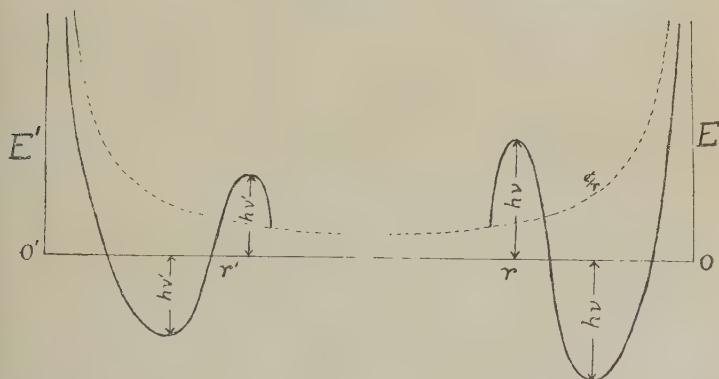
in the atoms are fixed. From this unstable state, the electrons will approach till the forces again attain equilibrium in a final stable position. The potential of the system at various distances is shown diagrammatically in fig. 2.

Returning to the doublets of fig. 1, the first point of importance is that electrostatic forces, however intense, of collision or of chemically active frequencies, will have no tendency to separate the constituent electrons. A doublet will scatter as a single particle with no effect on the bond. The only force affecting the two magnets differently is that due to a magnetic field normal to the axis of the magnets (perpendicular to the plane of the paper in fig. 1). When the natural period of oscillation is the same as that of an

incident radiation and sufficient amplitude attained, the similar poles will be brought into juxtaposition and the magnetic bond destroyed. The electrons will then move apart with an energy corresponding to their electrostatic potential at the point where magnetic equilibrium is reached. Radiation of the right frequency is the only means by which this bond can be destroyed.

The formation of a bond is the reverse process. The valency electrons, colliding with an energy equal to or greater than the critical potential energy of the bond, approach close enough for the magnetic attraction to predominate, and the compound is formed with absorption of the kinetic energy.

Fig. 2.



Consider, first, the simple case of uncatalysed dissociation or transformation, involving only one reactant molecule, in which the resultants are removed or do not react. This reaction is possible at any part of the molecular path, and its velocity depends simply on the energy density of the required radiation or that of the effective magnetic component. The observed effect of exterior illumination should be considerable, and, in fact, these reactions have provided the stock examples quoted by the adherents of the hypothesis. Several cogent arguments apply more particularly to such—*e. g.*, that reaction velocity is independent of dilution or expansion.

The simple act of combination is governed by entirely different factors. The electrons, constituting the bond, must be forced together, the electrostatic potential energy of the critical position being supplied at the expense of the kinetic

energy of thermal agitation. This must be in addition to the demands made by the elastic forces and radiation loss of an ordinary collision. The critical energy, w , may be identified as the critical increment which is used in deriving the Marcelin-Rice equation from the standpoint of thermal agitation. The expression AR/N is then equal to w and the velocity constant

$$k = se^{-\frac{A}{\theta}} = se^{-\frac{w}{\theta}}.$$

The equation derived from the radiation hypothesis is $k = se^{-\frac{h\nu}{\theta}}$, both being equivalent to the empirical law of Arrhenius $k = se^{-a/\theta}$. Hence w , the potential energy of the newly-made bond, which is sensitive to the frequency ν , is equal to the quantum $h\nu$. The probability of the formation of the bond is determined by the thermal agitation and the velocity of a simple combination should not be affected by radiation.

These conclusions may be used as a criterion for the effect of illumination in any actual reaction. Combinations generally involve rupture of the original bond, and, in that regard, another factor must be considered. The temperature radiation principally occurs during collisions, so that, during the time when only reaction can occur, the sensitive molecule is subjected to radiation of a local intensity enormously above the statistical value at the temperature of the mass. This must very largely increase the effectiveness of the temperature radiation as compared with illumination for this type of reaction, quite independently of the particular physical picture we are considering.

The complete process of a reaction, in general, involves a double process for each valency electron. It must first be freed from its original state by absorption of a resonant radiation, then forced into the new state by absorption of thermal energy $h\nu$.

In an exothermic reaction, the lower frequency of the old bond would probably reach a saturation value in impacts sufficient to form the new bond of higher critical energy, and the reaction velocity be determined by the latter predominantly or entirely.

When the energy quantum of the original bond is the greater, the absorption of radiant energy of the necessary frequency will largely determine the rate of reaction. As far as the temperature radiation is concerned, this will occur principally during collisions. The effect of illumination

should be marked, though the relative effects of the two types are not necessarily proportional to their statistical density. This will depend on the rate of dissipation of the oscillatory energy of the magnetons. In all types of reaction, however, selective absorption or emission of active frequencies should be observable.

This criterion seems to accord with the observed facts as to the reactions whose velocity is increased by illumination. In general, photo-catalysis should be observable where the rate of reaction is determined by a dissociation. In the objection brought forward by Lindemann (Phil. Mag. Nov. 1920), concerning the hydrolysis of saccharose by hydrochloric acid, the reaction which determines the velocity is the formation of an unstable compound, a *combination*, which dissociates into the resulting sugars at a much greater rate, presumably as the active frequency is abundant in the temperature radiation.

In the dissociation of ozone into oxygen, the velocity and equilibrium depend on the dissociation of O_3 and the reverse dissociation of O_2 , also on the corresponding combinations governed by thermal agitation. This reaction, at constant temperature, is, and should be, affected by radiation of frequencies corresponding to both these bonds.

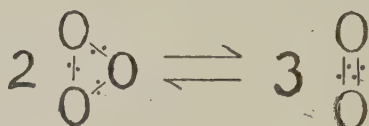
In the case of ionized compounds, it is presumed that electrons, superfluous to the stable system in the basic ion, have been transferred to complete that of the acid. This process may be regarded as the analogue of the combination in the former type of reaction. The compound is maintained by the general electrostatic attraction of the charged atoms, which corresponds to the force holding the valency electron to its nucleus in the unionized compounds.

The continued indication of quantum relations in such reactions suggests that the field of force, external to the atom, oscillates with the distance, giving definite positions of equilibrium. The frequency and energy of collisions should govern the combination and dissociation of such compounds, except in so far as they depend on the dissociation or combination of the constituent or resulting compounds of the former type.

Hence we see that this view of valency forces leads us to postulate, as a universal rule, quantum changes of energy in chemical reactions, with selective absorption and emission of the corresponding frequencies, but only in special cases, where the velocity is determined by the dissociation of an unionized compound, will any effect of exterior illumination

be observed. While giving due and equal importance to the two conflicting theories, it accords with the facts, qualitatively better than either, and quantitatively is generally identical.

In deriving this criterion for photo-catalysis, the critical state, which determines when the compound is made or destroyed, is the first unstable position of equilibrium in fig. 2. From this position, in the formation of a compound, it falls to the normal stable state with emission of radiation or, in dissociation, it is raised from that state by absorption of the characteristic frequency. If we assume that this corresponds to a change in potential of one quantum for each electron, the final energy change is the same as that postulated on the usual radiation hypothesis. The only difference is that the elementary energy change, $u = h(\nu - \nu')$, is associated, not with one molecule but with one valency bond. Thus, in the reaction of ozone \rightleftharpoons oxygen, which we may write,



six bonds characteristic of ozone are replaced by six of oxygen, and the energy liberated $U = 6H(\nu - \nu')$ per mol or $u = 3h(\nu - \nu')$ per molecule of ozone decomposed, ν and ν' being the frequencies which are absorbed by and destroy the valency doublets of oxygen and ozone respectively. In general, the various changes of valency linkages may be deduced from the stoicheometric formula, and the expressions for the velocity constant and heat of reaction will become

$$k = se^{-\frac{h}{k\theta} \Sigma \nu} \quad \text{and} \quad U = H(\Sigma \nu - \Sigma \nu').$$

The frequencies ν and ν' are spoken of throughout as single frequencies characteristic of the bond. The actual facts cannot be so simple. Different original states of the constituent electrons with respect to their nuclei, such as are necessary to explain ordinary radiation phenomena, must result in a series of such frequencies. Sub-multiple quanta will be introduced if the equilibrium states of the electrons with respect to each other are quantized in a manner analogous to the atomic states. Each frequency in this complicated series of probabilities will be drawn out into a

narrow band owing to the variations in natural period imposed by the proximity of other molecules.

It does not seem that any reaction is sufficiently well known to identify with safety a particular frequency with its corresponding valency bond. Various attempts have been made, different writers making different choices, but strict quantitative application can hardly be expected till more is known about the simpler phenomena of the characteristic frequencies of the atoms themselves.

With regard to the form in which the energy of reaction is liberated, it must be noted that the greater part is as radiation of a frequency which is selectively absorbed. A portion of this will escape, the remainder be absorbed by the newly-formed bonds in a non-radiating condition and dissipated only by collisions with other molecules. The observations of W. T. David (*Phil. Mag.* Nov. 1921) that the maximum of infra-red emission is attained, in explosions, earlier than the maximum temperature are in marked accordance with this view.

Another phenomenon to be expected is the alteration of U and ν by solvents in non-stoicheometric catalysis. The above hypothesis demands intense inter-molecular magnetic fields (Oxley, *Phil. Trans. A.* 215, p. 79), so that the surrounding molecules of the solvent would change the natural frequency and potential of the magnetic doublet.

The valency bond is inextensible, a condition which seems to be demanded by the evidence of the specific heats of diatomic gases at high temperature. Dissociation cannot be caused directly by the most violent impact or tension, save by ionization—*i.e.*, the attractive force between the magnetons is not affected, but one of them may be dislodged from its position in the atom.

This physical picture has proved valuable from so many points of view, and is supported by such a mass of evidence, chemical and magnetic, that it well deserves consideration in the not unreasonable expectation that it may be equally capable of explaining spectroscopic phenomena, which alone can define the necessary dynamical assumptions and put it to a crucial quantitative test.

XXXII. *On the Orientation of the Bohr-Sommerfeld Orbits.*
 By ARTHUR W. CONWAY, F.R.S., University College,
 Dublin*.

IN the Bohr-Sommerfeld theory of elliptic orbits about a simple centre of force a difficulty at once appears to present itself. Selecting any line as z -axis and taking the usual polar co-ordinates (r, θ, ϕ) , the properties of the nucleus or of the space about it seem to cease to be isotropic. The structure of the various orbits is symmetrical about the z -axis. In fact, the normal to the plane of any possible orbit makes an angle with the z -axis whose cosine is $n_2/(n_2+n_3)$ where n_2, n_3 are integers, being the partial azimuthal numbers. Or, put differently, the planes of all orbits which have the same azimuthal numbers envelope right circular cones. In what follows it will be shown that, by taking different coordinates, the orbits which have given azimuthal numbers touch a set of confocal quadric cones, the angle between the focal lines of which is at our disposal. The new coordinates, like the old (θ, ϕ) , are "separable." In fact, θ and ϕ are special cases. It is therefore necessary to add to Sommerfeld's criteria for the "selection" of orbits. It is necessary to specify the coordinates which have to be employed.

The cones

$$\frac{x^2}{a^2-\lambda^2} + \frac{y^2}{b^2-\lambda^2} + \frac{z^2}{c^2-\lambda^2} = 0$$

represent confocal cones, the focal lines being given by

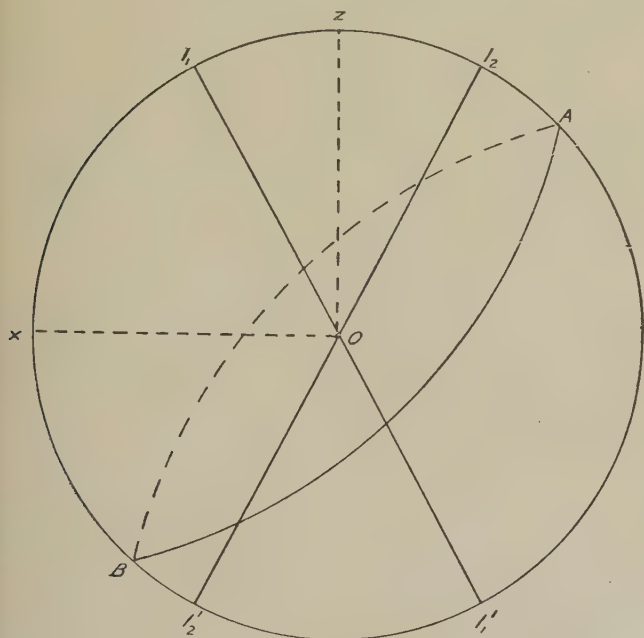
$$\frac{x^2}{a^2-b^2} - \frac{z^2}{b^2-c^2} = 0$$

($I_1 I_1'$ and $I_2 I_2'$ in the figure), where we take a, b , and c to be in descending order of magnitude. Through any point we have two values of λ^2 which we shall call λ^2 and μ^2 , such that $a^2 > \lambda^2 > b^2$; $b^2 > \mu^2 > c^2$. The μ -cones will surround OI_1, OI_2 and the λ -cones OI_2, OI_1' , with similar results for the other sheets of the cones. Let the plane of an orbit cut the circle of radius r through $I_1 I_2 I_1' I_2'$ in A and B. A certain μ -cone (μ_0) will touch this plane so that the whole range of μ for the orbit will be from $\mu=c$ to $\mu=\mu_1$, repeated four times. The range of λ will be from b to a repeated four times. Similar results will hold if A lies between I_1

* Communicated by the Author.

and I_2 . Taking as coordinates r, λ, μ we find for the square of the line-element

$$dr^2 + r^2(\lambda^2 - \mu^2) \left\{ \lambda^2 d\lambda^2 / (a^2 - \lambda^2)(b^2 - \lambda^2)(c^2 - \lambda^2) - \mu^2 d\mu^2 / (a^2 - \mu^2)(b^2 - \mu^2)(c^2 - \mu^2) \right\}.$$



If A is the Action Function we then get Jacobi's equation in the form

$$\frac{1}{m} \left(\frac{\partial A}{\partial r} \right)^2 + \frac{(a^2 - \lambda^2)(b^2 - \lambda^2)(c^2 - \lambda^2)}{m r^2 \lambda^2 (\lambda^2 - \mu^2)} \left(\frac{\partial A}{\partial \lambda} \right)^2 - \frac{(a^2 - \mu^2)(b^2 - \mu^2)(c^2 - \mu^2)}{m r^2 \mu^2 (\lambda^2 - \mu^2)} \left(\frac{\partial A}{\partial \mu} \right)^2 + \frac{2e^2}{r} - C = 0,$$

where m is the mass, $e, -e$ the charges on nucleus and electron, and $-C$ the energy constant. We then get the equations

$$\left(\frac{\partial A}{\partial \lambda} \right)^2 = mK \frac{\lambda^2(\lambda^2 - \mu_0^2)}{(a^2 - \lambda^2)(b^2 - \lambda^2)(c^2 - \lambda^2)},$$

$$\left(\frac{\partial A}{\partial \mu} \right)^2 = mK \frac{\mu^2(\mu^2 - \mu_0^2)}{(a^2 - \mu^2)(b^2 - \mu^2)(c^2 - \mu^2)},$$

where K is a constant. Hence, for the part of A which

depends on λ and μ we get

$$\begin{aligned} & \sqrt{mK} \int \lambda d\lambda \sqrt{\left\{ \frac{\lambda^2 - \mu_0^2}{(a^2 - \lambda^2)(\lambda^2 - b^2)(\lambda^2 - c^2)} \right\}} \\ & + \sqrt{mK} \int \mu d\mu \sqrt{\left\{ \frac{\mu_0^2 - \mu^2}{(a^2 - \mu^2)(b^2 - \mu^2)(c^2 - \mu^2)} \right\}}. \end{aligned}$$

Remembering the ranges of λ and μ we get the azimuthal equations

$$\begin{aligned} 2 \sqrt{mK} \int_{b^2}^{a^2} dz \sqrt{\left\{ \frac{z - \mu_0^2}{(a^2 - z)(z - b^2)(z - c^2)} \right\}} &= n_2 h, \\ 2 \sqrt{mK} \int_{c^2}^{\mu_0^2} dz \sqrt{\left\{ \frac{\mu_0^2 - z}{(a^2 - z)(b^2 - z)(z - c^2)} \right\}} &= n_3 h, \end{aligned}$$

where the variables λ^2, μ^2 have been changed to z . It will first be noticed that $n_2 h / \sqrt{mK}$ and $n_3 h / \sqrt{mK}$ are the periods of the elliptic integral

$$\int dz \sqrt{\left\{ \frac{(z - \mu_0^2)}{(a^2 - z)(b^2 - z)(c^2 - z)} \right\}}.$$

The sum of these periods is 2π , as may be seen by integrating with z , complex, about an infinite circle so that we get $(n_2 + n_3)h = 2\pi \sqrt{mK}$, from which the normal value of $-C$ can be deduced. Returning to the periods, they are certain transcendental functions of $\mu_0, f_1(\mu_0), f_2(\mu_0)$ (say), and so we have

$$f_1(\mu_0) = n_2 h / \sqrt{mK},$$

$$f_2(\mu_0) = n_3 h / \sqrt{mK},$$

$$\text{or } f_1(\mu_0) / f_2(\mu_0) = n_2 / n_3,$$

so that if n_2 and n_3 are given, μ_0 is given and the orbit must touch the quadric cone

$$\frac{x^2}{a^2 - \mu_0^2} + \frac{y^2}{b^2 - \mu_0^2} + \frac{z^2}{c^2 - \mu_0^2} = 0.$$

XXXIII. *The Physical Interpretation of Relativity Mathematics.* By C. H. BICKERDIKE *.

EINSTEIN, in Chapter XII. of his little book on Relativity, p. 36, referring to the Lorentz transformations, says: "*A priori* it is quite clear that we must be able to learn something about the physical behaviour of measuring-rods and clocks from the equations of transformation, for the magnitudes x, y, z, s, t are nothing more nor less than the results of measurements obtainable by means of measuring-rods and clocks." It is quite evident that he means that rods in motion relatively to the observer could be ascertained by measurement to be shortened and clocks in motion could be ascertained to go slower than similar clocks at rest if the necessary delicacy of observation could be attained. If he does not mean that, it is difficult to know what the passage above quoted can be intended to mean.

In the whole book, however, there is no explanation of how such measuring and observing of the effects could conceivably be made, even on the supposition that the necessary degree of delicacy of observation or high degree of velocity could be obtained, although Einstein quite freely makes use of such suppositions for the purpose of explaining some aspects of his theory.

It is commonly supposed that practical difficulties are all that stand in the way of testing the contractions and slowings-down. It is here submitted, however, that that is not the case, and that, in fact, there is a confusion in speaking of the Lorentz transformations as giving information about the "physical behaviour" of clocks.

It is necessary to point out first of all the fundamental distinction between observation of certain predicted effects deduced from the elaborated general theory of relativity, such as the motion of the perihelion of Mercury and the bending of light, and observation of the alleged physical interpretation of the meaning of the Lorentz transformations. These transformations—and the equations of the general theory—may, and doubtless do, express important truths. The question still remains, however, whether it is truth about the behaviour of light and of other electromagnetic phenomena involving transference of forces across "space" or the "æther," or whether the truths relate, as Einstein says, to the physical behaviour of measuring-rods and clocks. It is the

contention of the writer that at least as regards clocks and time the inference that the transformation of t and t' gives information as to their physical behaviour cannot be accepted.

So far as regards the main effect of the velocity of light in making the observations of one observer differ from those of another, it is easy to deduce from what is observed by S' what would be observed by S . There would be transformation equations connecting x and x' , t and t' , etc. No one suggests that these transformations are due to the physical behaviour of measuring-rods and clocks. It is found, however, that if we take the simple assumption of the constant velocity of light and the principle of moving axes, the transformation is not quite right. After allowing for the velocity of light as a constant, there is still a further small correction required, which is expressed by the Lorentz transformations. There is no *logical* necessity to assume that this transformation is consequent upon physical behaviour of clocks and rods. It may be that for some purpose of mathematical reasoning that assumption works sufficiently well. If it is to be taken literally, however, as a physical truth, the meaning in terms of what would be actually observed by numbers of observers in various circumstances, each recording what happened in his immediate environment, and subsequently comparing notes, requires to be explained before any clear meaning can be attributed to such phrases as physical behaviour of clocks and rods.

Eddington, in his 'Space, Time and Gravitation,' makes something like a realistic attempt to explain what the Lorentz transformations mean when translated into terms of what would be actually observed. It is submitted, however, that he stops short just at the point at which the explanation would begin to explain. His illustration of the aviator flying overhead at the convenient speed of 161,000 miles per second serves excellently to illustrate the point. The actual magnitude of the velocity is of no importance. The principle is exactly the same if we deal with smaller velocities. It saves time and trouble, however, to take the simplest illustration.

We are told, in the first place, that if he lay along the direction of his flight we on the ground should see him apparently only about three feet long, but the normal width—and he would have a strictly reciprocal impression of us if we lay on the ground in the direction of flight.

It is to be remarked that that is the only kind of *observation* of the effects of reciprocal motion which is ever definitely mentioned, and this relates only to contraction of length.

Eddington says, however, of the reciprocal shortenings : "It is not an illusion in the ordinary sense, because the impressions of both would be confirmed by every physical test or scientific calculation suggested." Presumably the "physical tests" must include measurements with clocks and rods. Yet we are never told how this could be done, and presently we shall see why.

It may be remarked in passing, however, as very interesting, that Eddington goes on to say : "No one knows which is right (*i.e.* the aviator or the observer on the ground), because we can never find out which, if either, is truly at rest in the ether." That seems to imply some clinging to the original idea of the FitzGerald-Lorentz contraction as a "real" contraction dependent upon absolute motion through the æther—*i.e.* motion relative simply to the æther and having nothing to do with motion relative to the observer. A contraction arising in that way might perfectly well be verifiable by measurement, but it would not be a strictly *reciprocal* effect of relative motion of two material bodies. In Einstein, there is no suggestion of clinging to this original conception of the FitzGerald-Lorentz contraction.

It is suggested that once the contraction is assumed to be a strictly reciprocal effect of relative motion, the whole idea of its being something physically measurable and verifiable is entirely destroyed. We have, however, first of all to consider further the question of the clocks.

Eddington's observer on the ground *calculates* that the aviator's clock goes slower than his own, and the aviator makes a similar calculation that the clock on the ground goes slow, and likewise each *infers* that the other's cigar is smoked more slowly than his own.

Eddington is careful to point out that the slowing of the clock is an inference and not an observation. "I say 'infer' deliberately ; we should *see* a still more extravagant slowing down of time ; but that is easily explained, because the aviator is rapidly increasing his distance from us and the light impressions take longer and longer to reach us. The more moderate retardation referred to remains after we have allowed for the time of transmission of light." The inference is therefore entirely dependent upon making the allowance for the velocity of light in the way which is assumed correct on the relativity principles, and this kind of observation therefore furnishes no possible means of verifying the correctness of the formulæ, or rather of the *interpretation* of the formula as giving information about the physical

behaviour of the clock and cigar when they are not immediately adjacent to the observer.

Eddington's discussion of the possibility of verification is confined to the question what would be observed if the aviator returned on his course, and he escapes the difficulty by pointing out that accelerations would have to be introduced and the discussion in question relates only to uniform motion.

For uniform motion—*i. e.* the restricted theory—the only possible verification can be by means of one or more additional observers stationary relative to the first.

If we introduce a second observer on the ground, the theory requires that, given what the first observer sees, in order to find what the second would observe, we have to imagine the origin of axes moved along to him from the first observer with the velocity of the thing under observation. That means, of course, that when the aviator passes over the second observer, the latter sees the aviator's clock showing just what the aviator himself sees.

In the absence of any discussion in books such as those of Eddington, Einstein's already mentioned, and Bolton's 'Introduction to the Theory of Relativity,' one might take it for granted that this means that the second observer would verify the calculation of the first observer, and, in fact, there can be no doubt that that is what is assumed to be the case, and that assumption is the foundation of what the public have regarded as the most striking mystery of the relativity theory.

It is submitted that the Lorentz transformation is open to a different interpretation. Before going into that, however, we will first consider some problems connected with circular motions. That means, of course, that we are no longer dealing with the restricted theory, and the reasoning about the reciprocal slowings of clocks is not quite the same.

The slowings connected with the restricted theory are not, however, something totally disconnected with the general theory. The restricted theory is a limiting case of the general theory, when gravitational fields are reduced to zero. If we start with no gravitational fields in existence and infer certain changes in lengths and times on the principle of the restricted theory, and then consider a case exactly parallel excepting that a small gravitational field is in existence, there is a difference between the changes of lengths and times to be inferred in the two cases, but a difference which must be proportionate to the strength of the field. We do

not, by introducing the gravitational field, suddenly abolish all the influence of mere relative motion.

Einstein, in his chapter on "The behaviour of clocks and measuring-rods on a rotating body of reference," indeed, begins his exposition by appealing to the results of the restricted theory. He supposes an observer on a Galileian reference system K (free from gravitational fields) to be observing a circular disk K' which is rotating, as judged by the observer on K . There is a clock at the centre of the rotating disk and one at the circumference. "As judged from this body (K), the clock at the centre of the disk has no velocity, whereas the clock at the edge of the disk is in motion relative to K in consequence of the rotation. According to a result obtained in Section XII., it follows that the latter clock goes at a rate permanently slower than that of the clock at the centre of the circular disk, *i.e.* as observed from K . It is obvious that the same effect would be noted by an observer whom we will imagine sitting alongside the clock at the centre of the disk."

From these facts Einstein *deduces* the inference that "in every gravitational field a clock will go more quickly or less quickly according to the position in which the clock is situated (at rest)."

In the case in question, the clock on the edge of the disk comes round again and again and can be observed from K over a period of time, and if the inference about slowing refers to "physical behaviour" of the clock, this slowing will be verified by the observer on K and would be also obvious to an observer alongside the clock on K' —who could see both his own clock and that of K at each moment of passing. It would then be properly described as a "real" slowing.

But we are equally entitled to say that, owing to the relative motion—which was the reason given for the slowing of the clock on K' —the observer on K' would infer that the clock on K went slow. The inference might not be that the *rate* of slowing inferred by K' with regard to K was exactly similar to that inferred by K with regard K' . There is not the exact reciprocity of the restricted theory. K' , however, would infer a slowing and not an acceleration of the clock on K , by reason of the relative motion, and one or other or both would be found wrong.

It may be replied that the clock on the rotating disk being fixed to the disk is subject to stresses, and that no one knows what would be the effect of such stresses.

That is not a satisfactory answer, it is submitted. In the first place, we do not know that stresses of this kind must produce *any* effect at all, and if they did it is hardly likely that time-measuring instruments of all kinds would be affected alike. The centripetal force has direction and can hardly be supposed to affect uniformly in all directions the motions of parts of a mechanism. Any mere mechanical errors of that kind, moreover, should be discoverable and capable of correction.

The whole theory is based on the assumption that time can be measured by some kind of clock. How, otherwise, can any meaning at all be attributed to the symbols t and t' ? The theory as expounded is represented as meaning that *time* goes slower on the moving system, in the sense that all activities are slowed, not merely those of a clock of a particular make. The slowing of time is supposed to affect the rate of motion of all kinds of clocks, of cigar smoking, and of the activities of living organisms, and of the rate of vibration of atoms and electrons.

It is submitted that in the case cited this cannot possibly be a real observable effect, since K and K' cannot each find, on their periodically meeting, that these activities are all going slower for the other than they are for himself.

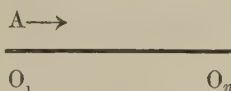
Let us take, however, the case of two equal disks rotating in opposite directions round the same axis with equal velocities, and let there be clocks fixed on the edge of each disk, with an observer at each. Now the centripetal forces or gravitational fields are of the same strength in each case and the magnitude of the stresses on the clocks is the same. How is it conceivable that, on the periodical juxtaposition of the two observers, each can see that the other's clock has gone slower than his own clock?

Another problem is this. Suppose K' rotates on an axis which is at rest relative to K , and there is a mark on the axis. K can measure time by the periodical passage of K' across this mark. K' can measure time by the periodical apparent alignment of himself between K and the mark. The instant at which K , K' and the mark would appear to be in a straight line would not be exactly the same for K and for K' , but the appearances of alignment would occur *with the same frequency* to both observers, and each can measure time by these recurrences. How, in that case, could it be said that "time" went slower for the one than the other? Why should not this phenomenon be the "clock" for each?

It is submitted that we are bound to look for some other meaning for the transformation of t and t' than "physical

behaviour" on the part of clocks, and incidentally that the inference from the general theory of relativity as to the slowing down of light-vibrations—the shift towards the red—need not be expected. If clocks do not slow down in any real sense, then vibrations of electrons not be supposed to so.

Reverting now to the restricted theory and Eddington's aviator. Let there be two observers on the ground, O_1 and O_n , the latter at a distance which would be covered by the aviator in 30 minutes, as measured by the clocks on the ground.



We have to ask what O_n , the second observer, would have to expect would be the time by the aviator's clock when the latter arrived at O_n . His origin of axes is, of course, on himself, and at the moment when O_n 's clock is at zero, he knows that the aviator is at a distance to the left, $-x$, moving towards him with a velocity V . He knows that O_1 's clock, at the same distance, but stationary, is at zero; but O_n does not agree that as between himself and the aviator it is zero time. He has to make his calculation as to what he "infers" to be the time by the aviator's clock. The velocities may be expressed in miles per minute, and the distance $-x$ is equal to $-30V$. According to the formula, t' the time "inferred" by O_n regarding the aviator's clock is

$$t - \frac{v}{c^2} x \quad \text{i. e.,} \quad \frac{0 + \frac{v^2}{c^2} 30}{\sqrt{1 - \frac{v^2}{c^2}}}$$

which comes to +15. According to O_n , therefore, when his own clock is at zero, that of the aviator is already at +15, and as the aviator's clock is inferred to go at half the speed of O_n 's own clock, O_n should expect it to show +30 minutes when the aviator arrives and therefore to agree exactly with his own clock at that instant.

The assumption that the second observer would verify the calculation of the first is based, one may conjecture, on a confusion about changing the origin of axes. When they are changed from O_1 to O_n , *with reference to observation and inference about the moving system*, the zero of time is changed in one sense i. e. O_n attributes to the position of O_1 a different zero, but only so far as regards time on the

moving system. The mental change which I make in transferring the axes to O_n does not alter the physical fact that the clock of the stationary observer O_1 is still at zero. O_1 and O_n can and do have their clocks at zero at what they are agreed is, by definition, the same time, and the physical facts about their clocks are adjusted accordingly without reference to the existence of any aviator.

The inference of O_n about the aviator's clock can be nothing but a mathematical fiction. O_n is not there to see it at that moment. It is a mere matter of difference of *definition* between O_1 and O_n as to what they are to regard as zero time as between each of them and the aviator, and that difference of definition has no effect on the physical state of the clocks unless and until the parties agree to adjust the clocks according to the definition.

The physical facts as to the aviator's clock cannot be made to accord with *both* the definitions about zero time as between himself and O_1 and O_n respectively. The clock was actually set to agree, at zero, with O_1 . As regards O_n , the "inference" about the clock of the aviator going slow has no meaning excepting that what was correctly *called* zero as between the aviator and O_1 has to be *called* +15 as between the aviator and O_n .

It is submitted that what O_n would directly observe would be that the aviator's clock was at +30 when he reached O_n . He would not make any direct observation which would confirm the calculation of O_1 .

If there were likewise two aviators exactly the same reasoning must apply to them. They would not confirm one another's inferences.

The upshot is that so long as we regard only what is *directly* observed by a number of observers, as to what is visible and tangible in his immediate neighbourhood, and put together the results, we get the ordinary world of Euclidean space and absolute time. If we compare this with the analogy of blind men, "judging" by sound, but arriving at a conception of real motions by putting together the direct observations in which the finite and sometimes variable velocities of sound are eliminated, we should say that the result of the direct observations is entitled to be called the "real" or "physical" truth. Similarly it would seem, that whatever may be the truth expressed by the Lorentz transformations, it cannot be understood in any intelligible sense, that the transformation of t and t' gives us information about the "physical behaviour" of clocks.

Another point which may be considered is this. The

calculation of O_1 is that the aviator's cigar is smoked at only half the rate of O_1 's own cigar. But suppose the aviator holds his cigar in the line of his motion. It is "judged" by O_1 to be only half the length of O_1 's own cigar. At the same time it is inferred to be smoked only half-way through by the time O_1 has finished his cigar. On that supposition should not we say that the aviator is judged as smoking at only a quarter of the rate of O_1 ?

This consideration prompts another question about the clocks. There is no inherent reason why a clock should not have a pointer moving along a straight line instead of in a circle. Suppose the clocks are of this kind, and that, at rest, the pointer measures time by covering one inch per minute. The aviator has his clock with the straight-line dial in the line of his motion. To O_1 it "appears" that each inch on the aviator's clock is only half an inch, and in that sense his clock may be said to appear to go at only half the rate of the clocks on the ground. But the theory as expounded by Eddington and Einstein appears to imply that it would cover only half as many spaces as the clocks on the ground, and it might be said that it appeared to go at only a quarter of the rate of those clocks.

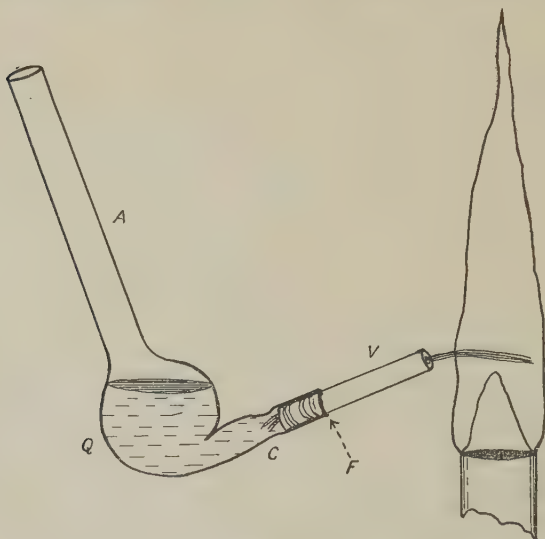
Should we not infer that the transformations embody some truth about the propagation of light between objects in motion relatively to one another and some truth about apparent contractions of length of objects in motion as seen by one observer only, who, therefore, can judge the length only by the apparent angle subtended, a contraction which, however, is not verified by comparison of observations by several observers, and which may be regarded therefore as analogous to an optical illusion—something additional to and different from what would be expected from the mere fact of the finite velocity of light?

The truth embodied respecting light implies also something about the state of the æther—or of space if we prefer that word—as affected by the motion of matter, and it is not surprising that this truth should have a bearing on all propagation of electromagnetic forces and also upon gravitation.

XXXIV. *On the Production of Coloured Flames for use with Spectrometers and Polarimeters.* By J. J. MANLEY, M.A., Research Fellow, Magdalen College, Oxford *.

THE apparatus represented in the accompanying figure has recently been designed and made for use with spectrometers and polarimeters. It is extremely convenient, requires but little attention, and by its means an intense flame coloration can be maintained for any desired period; the troublesome and unsatisfactory methods so frequently employed are thus entirely avoided. The apparatus is made in the following way:—

Near one end of a glass tube A about 1 cm. wide and 20 cm. long is first blown a bulb Q (fig. 1) having a capa-



city of 20 or 30 c.c.; then the short length of tube below the bulb is softened, drawn out, and bent at right angles to the larger limb A. In forming the narrower limb, care must be taken to make the diameter such that a portion of a "vitreosil" pipe V can be easily inserted. A suitable vitreosil pipe is one having a length of 8 cm., a diameter of 5 mm., and a bore of 1 mm. A constriction at C prevents the pipe from entering the tube for more than about 2.5 cm. The pipe with a few fibres of asbestos coiled upon it spiral-wise is introduced into the tube with a screw-like motion, the junction at F gently heated, and a little Faraday cement applied; a secure and liquid-tight union is thus effected. Finally, a bundle of 3 or 4 platinum wires, each 10 cm. long

* Communicated by the Author.

and 0.3 mm. in diameter, is placed within the pipe as shown. This bundle of wires constitutes a wick, the upper and free end of which is bent into a horizontal or even slightly downward position. Charging the bulb Q with the required solution and placing the exposed portion of the wick within a Bunsen flame as represented in the figure, an intense coloration is produced, and this as a result of the capillary action of the wires and pipe may be indefinitely maintained. If various flames are needed, it is convenient to construct several of the above-described feeders and to charge each with an appropriate solution: in this way the trouble caused by changing one solution for another and the cleansing of the apparatus, together with the consequent expenditure of time, may be avoided. The flame may be fed at very different rates by varying the inclination of the limb A. A suitable inclination, and therefore rate, is readily obtained by a corresponding rotation of the supporting clamp, which is not shown in the figure. To each solution should be added a very little hydrochloric acid. When the apparatus is not in use, A should be inclined so that a bubble of air appears at C.

Daubeny Laboratory,
Magdalen College,
Oxford.

XXXV. *The Effect of Gases in facilitating the Passage of Current from an Electron-Emitting Source in Crossed Electric and Magnetic Fields.* By Prof. O. W. RICHARDSON, F.R.S., and RABINDRANATH CHAUDHURI, M.Sc. (Calcutta), King's College, London*.

IT is well known that the passage of electron currents in vacuum tubes is stopped by the application of comparatively weak magnetic fields in directions perpendicular to the electric intensity. This is due to the curling up of the electron paths by the magnetic field, so that they intersect the emitting surface instead of extending to the anode. If, however, a trace of gas be admitted, so that the vacuum is no longer perfect, we find that the current will flow again, although its magnitude will in general be less than that obtained in the absence of a magnetic field. This effect occurs below the ionizing potential of the admitted gas, and therefore has nothing to do with the similar effect which occurs at higher potentials, owing to the formation of ions by impact ionization. The effect may be due to the combination of the electrons with neutral gas molecules to

* Communicated by the Authors.

form heavy negative ions (atomions), which pass to the anode, since their motion is little influenced by the magnetic field. However, it appears that almost anything which occurs at a collision will prevent an electron from returning to the emitting surface, in the type of apparatus used in our experiments at any rate; so that the passage of the current in a magnetic field is probably a test for any electron which has undergone a collision with a gas molecule, and not necessarily for one which has combined to form a negative ion. This should be borne in mind in reading the sequel, where the term "heavy ions" is sometimes used as an abbreviation for the "carriers of the current which succeed in reaching the anode in a transverse magnetic field great enough to stop the passage of electrons." These carriers behave from the experimental point of view like heavy ions would, and it is convenient to have a name for them; but we do not at this stage wish to commit ourselves definitely in all cases as to the detailed mechanism of the phenomena dealt with, and the name may turn out to be misleading.

We shall now consider the conditions which govern the passage of electrons between the electrodes in the absence of gas. The source of electrons was a tungsten filament of circular section (radius a) stretched along the axis of a cylindrical anode (radius b). The electric field (potential difference V) was applied between the hot wire and the anode, and the magnetic field H was parallel to the filament, so that the electric and magnetic fields were perpendicular to each other. Under these circumstances the electrons describe a curve similar to a cycloidal spiral about the filament, and the greater the magnetic field the less will be the maximum distance from the hot wire attained by an electron. The radial force due to the electric field at distance r from the axis can be written Ae/r when $A = V \text{ (volts)} \times 10^8 / \log \frac{b}{a}$.

Due to the current required to heat the filament (j amp.) there will be a magnetic field distributed in circles about the axis whose intensity is $\frac{B}{r} = \frac{2j}{10r}$. The equations of motion of the electron under these forces and that arising from the magnetic field H , parallel to the axis of z , will be

$$m \left[\frac{d^2 r}{dt^2} - r \left(\frac{d\theta}{dt} \right)^2 \right] = \frac{Ae}{r} + He \left(r \frac{d\theta}{dt} \right) - \frac{Be}{r} \frac{dz}{dt}, \quad (1)$$

$$m \left[\frac{1}{r} \frac{d}{dt} \left(r^2 \frac{d\theta}{dt} \right) \right] = -He \frac{dr}{dt}, \quad \dots \dots \dots (2)$$

$$m \frac{d^2 z}{dt^2} = \frac{Be}{r} \frac{dr}{dt} \dots \dots \dots (3)$$

Integrating (3) subject to $\frac{dz}{dt} = w_0$ when $r = a$ and (2) subject to $\frac{d\theta}{dt} = \dot{\theta}_0 = \frac{v_0}{a}$ at $r = a$, and substituting the values thus obtained for $\frac{dr}{dt}$ and $\frac{d\theta}{dt}$ in (1), gives

$$\frac{d^2r}{dt^2} = -\left(\frac{He}{2m}\right)^2 r + \left(av_0 - \frac{Hea^2}{2m}\right)^2 \frac{1}{r^3} + \frac{1}{r} \left[\frac{Ae}{m} - \frac{Bew_0}{m} - \frac{B^2e^2 \log \frac{r}{a}}{m^2} \right], \quad (4)$$

$$= Lr + M \frac{1}{r^3} + N \frac{1}{r}, \text{ say.} \quad (5)$$

On multiplying by $\frac{dr}{dt}$ and integrating, subject to the condition $\frac{dr}{dt} = u_0$ when $r = a$,

$$\left(\frac{dr}{dt}\right)^2 = L(r^2 - a^2) - M\left(\frac{1}{r^2} - \frac{1}{a^2}\right) - 2N \log \frac{r}{a} + \left(\frac{Be}{m} \log \frac{r}{a}\right)^2 + u_0^2. \quad (6)$$

But, at the maximum distance of the electron from the axis, $\frac{dr}{dt} = 0$. If r be now taken as this maximum distance, then

$$L(r^2 - a^2) - M\left(\frac{1}{r^2} - \frac{1}{a^2}\right) + 2N \log \frac{r}{a} + \left(\frac{Be}{m} \log \frac{r}{a}\right)^2 + u_0^2 = 0. \quad (7)$$

Putting in the values of L, M, and N from (4) and (5),

$$\begin{aligned} & \frac{H^2}{4} \left(\frac{e}{m}\right)^2 r^2 \left(1 - \frac{a^2}{r^2}\right)^2 + \frac{Heav_0}{m} \left(1 - \frac{a^2}{r^2}\right) \\ &= 2 \log \frac{r}{a} \left[A \frac{e}{m} - \frac{Bew_0}{m} - \frac{B^2e^2}{2m^2} \log \frac{r}{a} \right] \\ & \quad + v_0^2 \left(1 - \frac{a^2}{r^2}\right) + u_0^2, \quad (8) \end{aligned}$$

or, substituting the values of A and B in terms of V the

340 Prof. Richardson and Mr. Chaudhuri on the *Effect of* applied voltage and j the heating current in amperes,

$$\begin{aligned} \frac{H^2}{4} \left(\frac{e}{m} \right)^2 r^2 \left(1 - \frac{a^2}{r^2} \right)^2 + \frac{Heav_0}{m} \left(1 - \frac{a^2}{r^2} \right) \\ = \frac{2V \cdot 10^8 \cdot \frac{e}{m} \log \frac{r}{a}}{\log \frac{b}{a}} - \frac{2j}{5} \frac{e}{m} w_0 \log \frac{r}{a} \\ - \frac{1}{25} j^2 \left(\frac{e}{m} \right)^2 \left(\log \frac{r}{a} \right)^2 + v_0^2 \left(1 - \frac{a^2}{r^2} \right) + u_0^2. \quad (9) \end{aligned}$$

This equation, if solved for r , gives the maximum distance which electrons, or ions, having a given value of e/m can get from the wire for given values of H and V . If in addition we put $r=b$, we shall get the limiting relation between H and V which must hold in order that an ion starting from the filament may reach the surrounding electrode.

As it stands, equation (9), regarded as an equation for r , is not a very simple affair. It happens, however, that with the values of H and j employed in the experiments the various terms have very unequal values. The term linear in H and the term in j^2 are negligible, and the term in j is relatively small. To a first approximation we can also treat $\frac{a^2}{r^2}$ as small compared with unity. To this approximation, after putting in the numerical values for a , b , and e/m , equation (9) reduces to

$$H^2 = \frac{8 \cdot 39 V \log r / \cdot 005}{r^2} + 89 \frac{V_1}{r^2}. \quad \dots \quad (10)$$

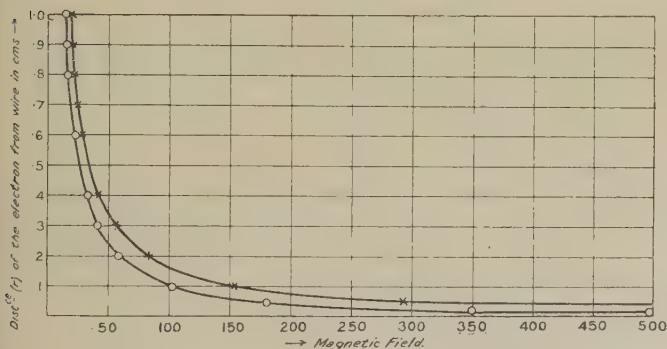
The values of H corresponding to different values of r given by this formula are shown in Table I. for V (the applied potential) = 4.2 volts and V_1 (the voltage equivalent of the emission velocity) equal to 0, 0.75, and 1.5 volts. The maximum emission velocity which is possessed by a measurable number of electrons is about 1 volt, and 1.5 volts can be safely taken as an upper limit for it. These values are only approximately correct, but they are accurate enough for the purpose of the present discussion. Any desired degree of accuracy can be obtained by keeping in more terms of equation (9) and proceeding in the same manner. Corresponding values of H and r for $V_1=0$, points \bigcirc , and $V_1=1.5$, points \times , are plotted in fig. 1.

TABLE I.

Applied Potential (accelerating) = $V=4.2$ volts.

Value of r .	Magnetic fields required to bring the electron of different initial velocities to r .		
	H for $V_i=0$.	H for $V_i=0.75$.	H for $V_i=1.5$ volt.
1.0 cm.	13.70	15.9	18.0
0.8	16.7	19.6	22.1
0.6	21.6	25.5	29.0
0.4	31.07	37.2	42.4
0.3	40.04	48.4	55.3
0.2	57.00	70.8	81.1
0.1	102.07	131.3	154.6
0.05	180.1	243.2	293.0
0.02	350.0	537.6	674.0
0.01	495.0	955.0	1260.0

Fig. 1.



From this figure we see that if a magnetic field of 160 units is used and the accelerating voltage between the filament and the cylinder is 4.2, the maximum velocity electrons will be confined within a distance of 0.096 cm. and the zero velocity ones within a distance of 0.06 cm. from the axis. This is on the supposition that the free movement of the electrons is not interfered with. If, however, the apparatus contains gas at a low pressure, encounters with gas molecules will occur, and as a result of such an encounter one of two things may happen. Either the electron will combine with the gas molecule to form a heavy ion which will travel to the anode in a slightly curved path under the combined fields—it would require a magnetic field of about 4000 units to stop an ion formed by the combination of a nitrogen molecule and an electron under these conditions,—or it will

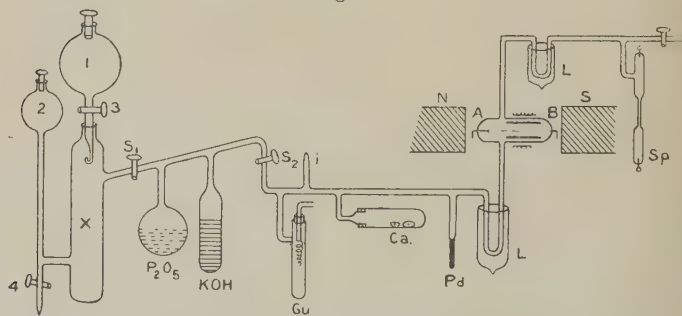
have its velocity suddenly altered so as to cause it to start to execute a new spiral path about an axis parallel to the magnetic field. The new path will not in general intersect the surface of the filament so that the electron will not return to the cathode, but neither will it intersect the surface of the anode. It will, however, in general be possible for such an electron to reach the anode as a result of a number of subsequent collisions. Thus we see that if gas is present, it will be possible for electrons to get through the magnetic field to the anode as a result of successive collisions with molecules as well as by combining with them.

Another advantage, as will be seen from fig. 1, of using fields as high as 160 units, is that the maximum distance of the electron and the corresponding length of the path is not very susceptible to small changes in the strength of the magnetic field in this region.

Experimental Arrangements.

The apparatus consists of a thermionic tube AB (fig. 2) placed axially between the poles of an electromagnet NS. The tube AB is connected on the one side with the gas-

Fig. 2.



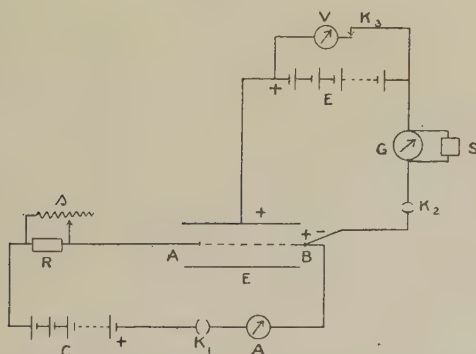
generating apparatus, and on the other with the spectrum tube Sp. and a phosphorus-pentoxide bulb, a mercury pump, and a McLeod gauge. On the two sides of AB are also two liquid-air traps LL.

The gas-generating part of the apparatus includes a palladium tube Pd for admitting hydrogen, a quartz tube containing two porcelain boats Ca containing calcium for absorbing gases, a glass tube Cu containing a spiral of copper wire which can be electrically heated for absorbing oxygen, and a set of apparatus X for generating nitrogen and other gases.

The thermionic tube AB consists of a cylindrical anode of thin copper 3.8 cm. long and 2 cm. in diameter, rigidly fixed in a glass tube. The cathode is a tungsten wire 3 cm. long and 0.01 cm. in diameter. By means of a suitable bow-spring, not shown in the figure, it is stretched taut along the axis of the cylinder, both when it is heated as well as when it is cold. In the preliminary preparation of the tubes the glass walls were heated as high as possible and the anode bombarded by an electron current from the hot wire whilst the gas was pumped away. Tests have also been made on similar tubes prepared by exhaustion in a vacuum furnace and then sealed off.

The electrical circuit is shown in fig. 3. The current for heating the filament AB is supplied by the battery C controlled by the resistance R, for which the shunt rheostat S

Fig. 3.



supplies a fine adjustment. The voltage driving the thermionic current is supplied by the battery E, the positive terminal of which is connected through the galvanometer G to the positive end of the hot wire. The potential difference between this point of the circuit and the anode is measured by the voltmeter V. The galvanometer G, used for measuring the thermionic current, had a sensitiveness of 1 division for 3×10^{-10} amp. For the larger currents the sensitiveness was reduced by means of the shunt S.

The magnetic field was produced by a large electromagnet. By varying the current through it the field between the poles, at 12 cm. distance, can be increased up to 1200 units. Before putting the tube AB in position, the field between the poles was explored. It was found that there was a residual field of about 10 units, and that when the current

was on, the field within 2 or 3 cm. on either side of the point midway between the poles was fairly constant.

The magnetic fields were measured by a coil and a fluxmeter. The coil used to measure the magnetic fields employed during the experiments consisted of 45 turns of silk-covered wire, wound on a cardboard cylinder which could be slipped over the thermionic tube AB. Before the tube was set up a certain magnetic field was established between the poles of the electromagnet and measured, using the standard coil supplied with the fluxmeter. The throw of the fluxmeter when the experimental coil was suddenly moved out of this same magnetic field was then measured. As a result of these measurements, it was found that 1 mm. deflexion of the scale, using the fluxmeter in combination with the experimental coil, was equivalent to 2 units of magnetic field, as nearly as the measurements could be made.

Preliminary Tests.

Before proceeding to the actual experimental tests, it is necessary to make sure that the tubes have been properly prepared. Tubes which have not been properly prepared are characterized by the possession of either or both of two defects. The first of these is the emission of positive ions and the second the emission of heavy negative ions, from the hot wire, under apparently good vacuum conditions. Both these conditions are readily recognized by carrying out preliminary experiments in the absence of gas, *i. e.* with as good a vacuum as the pumps used will maintain.

(1) *Positive ions.*—To test for these, reverse the potential of the battery E in fig. 3 so as to charge the cylindrical electrode negatively. Owing to the fact that the battery E is connected to the positive end of the hot wire and partly also to the emission velocities, if the applied potential difference V is small there will be a current through the galvanometer, which, however, will flow against the apparent applied electromotive force. This is due to the electrons, and will happen whether positive ions are present or not. If there are only electrons present, this current will fall sharply as the magnitude of V increases, and will, under our working conditions, disappear when V becomes equal to about -3 volts, and for greater negative voltages the current will remain zero. This is not the case if positive ions are present, for we then get a current carried by the positive

ions which flows in the direction of the applied electromotive force. Moreover, this latter current is unaffected by the application of a magnetic field, whereas the former is cut down to a small, or zero, value. The following numbers were given by a tube showing typical positive ion trouble:—

No magnetic field.

Applied Voltage.	0	-0.5	-1.0	-1.5	-2.0	-3.0	-4.0	-5.0	-6.0	-7.0
Current Reading.	24.1	22.8	13.8	3.9	0.8	-1.1	-1.7	-2.3	-2.5	-2.7

H=1000.

Applied Voltage.	0	-1	-2	-3	-4	-5	-6	-7	-8	-9
Current Reading.	0.0	0.0	-0.1	-0.6	-1.1	-1.5	-1.8	-2.0	-2.2	-2.3

If no positive ions had been present, all the negative values of current readings in the upper part of this table would have been zero, and all the current readings would have been zero in the lower table.

(2) *Negative ions.*—If these are present there will be a current to the anode, under high-vacuum conditions, in a strong magnetic field when the cylindrical electrode is positively charged, *i. e.* when the battery E is applied in the usual way. The following are typical data for a tube having this defect:—

H=1000.

Applied Voltage.	0	+1	+2	+3	+4	+5	+6	+7	+8	+10
Current Reading.	0.9	2.5	4.0	4.5	5.0	7.5	11.0	15.0	19.0	29.0

If no heavy negative ions had been present, the current readings would have all been zero under the conditions above.

In a properly prepared tube the phenomena just described are absent. Almost all the current from the hot wire to the electrode is carried by electrons. If a magnetic field is put on, the residual current will be very small if the pressure of the gas is small. This has previously been established by Owen and Halsall* with wires of iridium, palladium, and platinum, and by Richardson† with platinum. The following

* Phil. Mag. vol. xxv. p. 735 (1913).

† Loc. cit. vol. xxvi. p. 458 (1913).

346 Prof. Richardson and Mr. Chaudhuri on the *Effect of* table gives typical results obtained by us with tungsten in presence of traces of air and nitrogen :—

TABLE II.

Applied Potential 4·3 volts. Magnetic Field $H=160$.

Residual gas.	Pressure mm. of mercury.	Saturation Current without magnetic field. amp.	Residual Current with magnetic field. amp.	Current carried by electrons. amp.
Air	3×10^{-5}	$3600 \times 3 \times 10^{-10}$	$0.2 \times 3 \times 10^{-10}$	$3599.8 \times 3 \times 10^{-10}$
Air	6×10^{-5} „	4800 „	0.5 „	4799.5 „
N ₂	10^{-4}	700 „	0.3 „	699.7 „

The following table gives data for a typical tube which has been satisfactorily prepared :—

TABLE III.

Gas pressure 10^{-4} mm.

Applied Potential.	Current without magnetic field.	Current with magnetic field $H=500$.
—6.0 volts	$0.0 \times 133 \times 10^{-10}$ amp.	0.0
—5.0 „	0.0 „	0.0
—4.0 „	0.0 „	0.0
—3.0 „	0.5 „	0.0
—2.5 „	7.0 „	0.0
—2.0 „	24.0 „	0.0
—1.5 „	56.0 „	0.0
—1.0 „	68.0 „	0.0
—0.5 „	76.0 „	0.0
0.0 „	77.0 „	0.0
+1.0 „	77.5 „	0.0
+2.0 „	77.7 „	0.0
+3.0 „	77.9 „	0.0
+4.0 „	79.0 „	$0.2 \times 2 \times 10^{-8}$ amp.
+5.0 „	80.0 „	0.3 „

Initial amounts of heavy ions sensibly greater than in the proportion indicated by the figures at the bottom of the last column are inadmissible, and if they are present, further preparation of the tube should be proceeded with.

Experiments in Air.

The tungsten filament was 2.8 cm. long and 0.01 cm. diameter, the surrounding cylinder being 3.8 cm. long and

2 cm. diameter. The tube was first prepared so as to satisfy the tests described above on pumping out the gas to a pressure of 0.0001 mm. or less. On admitting air to a pressure of about 0.03 mm., currents were found to flow in the presence of a magnetic field. When these tests were made shortly after the tubes were prepared, the currents in a magnetic field were found to be somewhat irregular and to change with continued heating of the filament. The pressure of the gas was also found to change at the same time, probably owing to the absorption of oxygen by the hot tungsten. After letting in fresh air at a low pressure several times and heating the filament whilst pumping the air out, the filament seems to get seasoned to it, so that comparatively steady conditions may be obtained. We suggest that this may be due to the formation of a protective coating of oxide over the surface of the tungsten. The next table shows a set of typical figures obtained under these conditions.

TABLE IV.

Heating Current of the filament = 1.0 amp.

Applied Potential (accelerating) = 4.2 volts.

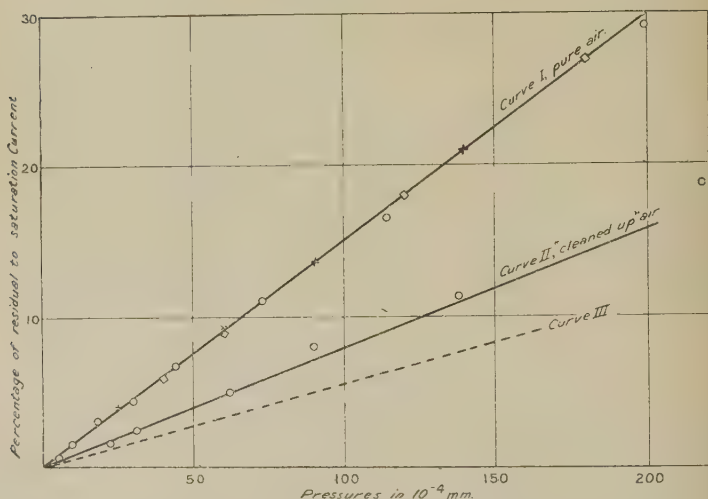
Pressure inside the tube.	Saturation Current without magnetic field.	Residual Current with magnetic field.	Magnetic Field.	Percentage of Residual to Saturation Current.
198×10^{-4} mm.	$2160 \times 3 \times 10^{-10}$ amp.	$630 \times 3 \times 10^{-10}$ amp.	164	29.2
114 "	2280 "	370 "	162	16.2
73 "	2280 "	250 "	162	11.0
44 "	2280 "	155 "	164	6.8
30 "	2280 "	100 "	162	4.8
18 "	2280 "	70 "	162	3.0
9 "	2340 "	35 "	162	1.5
5 "	2280 "	13 "	162	0.5

The maximum distance the electrons can get from the wire with the magnetic field used is a little under 0.1 cm., whereas the distance of the anode from the axis is 1 cm. The values at different pressures in the last column of this table are plotted against the pressure in Curve I., fig. 4, points O. It will be seen that the percentage is very closely proportional to the pressure of the gas. The other points near Curve I., viz. □ and ×, represent other series of observations taken under similar conditions.

If the wire is heated for a long time in the same air, the

percentage at a given pressure tends to diminish. This is probably due primarily to the absorption of the oxygen, but it may be due to some extent to the absorption of nitrogen also. A typical set of data after heating in air for a long time before taking the observations at successively lower

Fig. 4.



pressures is shown in fig. 4, Curve II. The dotted Curve III. of fig. 4 shows the lowest values of the percentage which we have been able to get in this way.

Experiments in Nitrogen.

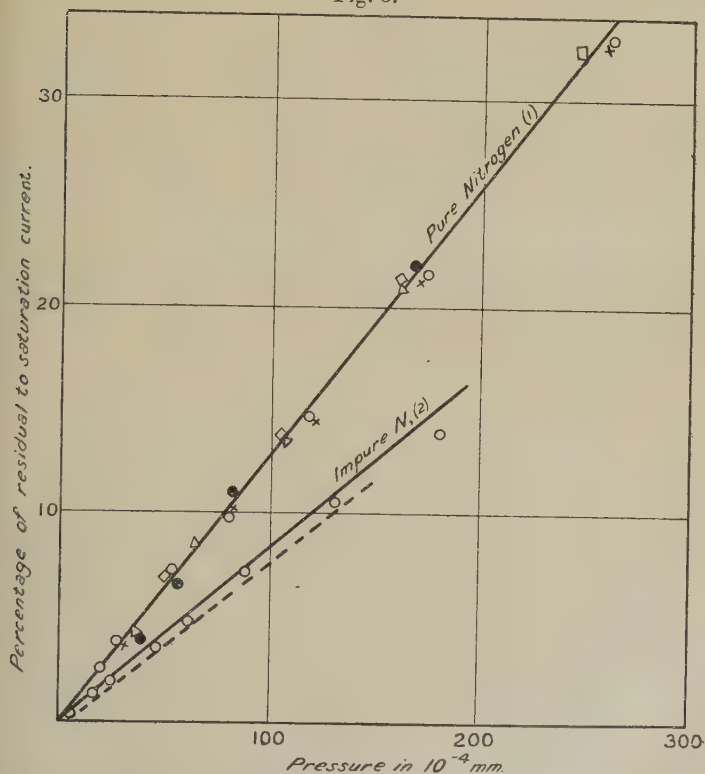
Two samples of this gas were tried, the first being commercial nitrogen supplied in cylinders by the British Oxygen Co., and the second nitrogen prepared chemically from ammonia.

When nitrogen was first admitted, similar phenomena were observed to those recorded with air. The pressure was found to diminish when the filament was heated and the anode bombarded with about 300 volts. After letting in fresh nitrogen a number of times and pumping it out with the filament hot, it was found that the pressure remained fairly constant under the experimental conditions.

A typical set of data got from the commercial nitrogen are shown in Curve II. of fig. 5. The heating current through the filament was 1.2 amp., the applied accelerating potential 4.3 volts, and the magnetic field ranged between

164 and 168 units. The percentage of residual to saturation current obtained with a given pressure of this sample of gas varied a little in the different experiments, doubtless owing to changes in the composition of the gas owing to the action of the hot filament on it. We have not analysed the gas,

Fig. 5.



but it probably contains argon and some traces of oxygen. The dotted line in fig. 5 shows the lowest set of values which we obtained with this nitrogen.

The chemical nitrogen was prepared in the apparatus shown in fig. 2. Pure ammonia solution was poured into vessel 2, which was filled up to the stopcocks 3 and S_1 . Pure bromine water previously boiled was placed in bulb 1 and poured into X by opening 3. The interaction produces nitrogen, which collects in the top portion of X. When X is about half full of nitrogen, S_1 is opened and the gas passes into the drying compartment. This dried gas is pumped

through the rest of the apparatus, and the process repeated several times before the sample of nitrogen which it is finally intended to test is stored in the compartment containing the phosphorus pentoxide and caustic potash. These agents remove any water vapour, ammonia, and bromine which may be mixed with the nitrogen. This convenient apparatus for preparing nitrogen free from air has been described by Waran*.

The stored nitrogen is let into the main testing apparatus in small quantities, the copper spiral being heated to take out any traces of oxygen which may have come from dissolved air in the liquids. Liquid air is kept on the traps to prevent access of bromine, ammonia, grease, mercury vapour or other vapours to the filament. The filament is heated, and the nitrogen let in and pumped out several times to get rid of any other occluded gases which may be present in the apparatus and to season the filament. The following data represent the result of a typical experiment made in this way:—

TABLE V.

Heating Current 1.35 amp.
Applied Potential (accelerating) 4.2 volts.

Pressure of Nitrogen.	Saturation Current without magnetic field.	Residual Current with magnetic field.	Magnetic Field.	Percentage of Residual to Saturation Current.
260×10^{-4} mm.	$522 \times 3 \times 10^{-3}$ amp.	$172 \times 3 \times 10^{-10}$ amp.	162	33.0
173 "	552 "	120 "	160	21.7
118 "	612 "	90 "	160	14.7
80 "	606 "	60 "	164	9.9
54 "	630 "	45 "	164	7.1
28 "	630 "	24 "	168	3.8
20 "	672 "	17 "	164	2.5

The values in the last column are shown plotted against those in the first, points O, close to the top line in fig. 5. Data given by four additional tests with nitrogen prepared in this way are also given. These data are all consistent with one another, and fall quite close to the line drawn. It will be observed that, for a given pressure, the percentage in pure nitrogen is greater than in the commercial nitrogen;

* Phil. Mag. vol. xlii. p. 246 (1921).

it is furthermore intermediate between the values for pure air and for air which has been "cleaned up" by tungsten (fig. 4).

Conclusion.

The most interesting results of this investigation up to the present are the comparatively large magnitudes of the currents in the magnetic fields, the proportionality of these currents with the gas pressures, and the relative magnitudes of the effects in air and in nitrogen. These data would seem adequate to settle the nature of the phenomena in its main outlines. The fact that the residual currents are of similar magnitude in air and nitrogen suggests that the formation of heavy ions is a relatively unimportant factor. If it were important we should expect the effect to be much more marked in air, since oxygen is a much more electronegative gas than nitrogen. We are thus led to the conclusion that the passage of the currents in the magnetic field is a test of a collision between an electron and a gas molecule simply, and not of a collision which results in combination of the two to form a heavy ion.

The proportionality between the residual current and the gas pressure seems at first sight a difficulty on this view; on the ground that the co-operation of more than one collision is required for an electron to reach the anode. This suggests that the effect might be expected to increase more rapidly than as the first power of the pressure. It is probable, however, that this view of the phenomena is too superficial. The first collision will really decide the fate of the electron, because it puts it in a condition which prevents it from being returned to the cathode by the magnetic field. Since the experiments deal with a steady state, there is no opportunity for indefinite accumulation of electrons or ions in the field; so that the only alternative is for the electron to reach the anode. If the gas present is inadequate to ensure this by means of collisions, it seems likely that the electrons present in the space will cause a readjustment of the electric field in such a way as to make this possible. On this view, the currents to the anode in a magnetic field will be proportional to the probability of a single collision, and therefore proportional to the gas pressure, for small pressures.

The actual magnitudes of the currents in a magnetic field are also consistent with this point of view. On the assumption that the occurrence of a single collision is sufficient to determine the passage of an electron to the anode, we can

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estimate a value for the mean free path of an electron in the gas. To do this, we require to know the length p of the path of an electron in the magnetic field when no collision occurs. As an approximate illustration let us take this to be an arc of a circle whose diameter is along the axis of the cylinders, and whose radius is equal to the maximum distance r which the electron travels from that axis. Then

$$p = r(\pi - 2 \sin^{-1} a/r),$$

a being the radius of the hot wire. The proportion of any group of electrons which travel a distance x without collision and then collide in the succeeding distance dx is

$$e^{-\frac{x}{\lambda}} \frac{dx}{\lambda},$$

and the proportion ξ which collide in a path of length p is thus

$$\int_0^p e^{-\frac{x}{\lambda}} \frac{dx}{\lambda} = 1 - e^{-\frac{p}{\lambda}}.$$

Thus

$$\lambda = -p / \log_e(1 - \xi).$$

For $H=160$, r lies between the limits 0.06 and 0.096 cm. according to the value of the initial velocity of the electron. If we take $r=0.08$ cm. as a mean value, this gives $p=0.08 \times 3.015$ cm. At a pressure of 0.02 mm. of mercury the value of ξ was 0.259.

On substituting these numbers, we find

$$\lambda = 0.805 \text{ cm. at } 0.02 \text{ mm. pressure,}$$

$$\text{or } \lambda_0 = 2.1 \times 10^{-5} \text{ cm. at } 760 \text{ mm. pressure.}$$

The last number is similar to those given by other methods. On account of the approximate nature of some of the assumptions made, no correction has been applied for the influence of the high temperature of the gas on its density under a given pressure.

If the preceding interpretation of the phenomena is substantiated by further experiments, it would seem that the method might be used to compare and perhaps to measure the mean free paths of electrons in different gases. Further experiments extending to a number of gases are in progress by one of us (R. C.), and will be reported upon shortly.

XXXVI. *The Ionization by Collision of Hydrogen, Nitrogen, and Argon.* By T. L. R. AYRES, B.A., M.Sc., *Exeter College, Oxford* *.

1. **T**HE principal object of these experiments was to determine the ionization in hydrogen, nitrogen, and argon, by collisions of electrons with molecules for comparatively small values of the ratio of the electric force X to the gas-pressure p . The range specially examined is from $\frac{X}{p} = 5$ to $\frac{X}{p} = 60$, X being in volts per centimetre and p in millimetres of mercury.

In the original determinations of the number of ions generated by collision in these gases †, the effects of positive and negative ions were not measured in cases where the values of $\frac{X}{p}$ were less than about 40.

The velocities in the direction of the electric force, and the mean velocity of agitation of the electrons in these gases, have been found recently by Professor Townsend and Mr. V. A. Bailey ‡ by a method which had previously been used to determine the motion of electrons in air.

Their range of investigation extended from $\frac{X}{p} = 0.25$ to $\frac{X}{p} = 60$ or 100; consequently, the determination of the number of ions generated by collision within this range is an allied question of considerable interest.

The number of ions generated by collisions of electrons with molecules, and the total number of collisions of electrons with molecules, would then be known for cases in which the mean velocity of agitation and the mean velocity in the direction of the electric force can be measured accurately.

When the original researches on ionization by collision were published, the term "ion" was generally applied to any small particle with an atomic charge, and included

* Communicated by Prof. J. S. Townsend, F.R.S.

† J. S. Townsend, *Phil. Mag.* iii. p. 557 (June 1902), and (6) vi. p. 598 (Nov. 1903). H. E. Hurst, *Phil. Mag.* (6) xi. p. 535 (1906). E. W. B. Gill and F. B. Pidduck, *Phil. Mag.* xvi. pp. 280-290 (Aug. 1908).

‡ J. S. Townsend and V. A. Bailey, *Phil. Mag.* xlii. p. 874 (Dec. 1921), xliii. p. 593 (Mar. 1922), and xliv. p. 1033 (Nov. 1922).

electrons as well as particles with masses of the order of the mass of a molecule.

At present, the term "ion" is generally applied only to the larger particles in order to distinguish them from electrons.

For brevity, it is frequently desirable to retain the original notation; so that when a pair of ions are said to be generated by a collision, what is meant exactly is that a positive ion and an electron are generated when a positive ion or an electron collides with a molecule. The original experiments afford ample evidence that with these forces and gas-pressures the electrons move freely, and are not combined with molecules of the gas. Also the ratio of the charge to the mass of the negatively charged particle shows that in the process of ionization by collision the negative particles which move along the free paths between collisions with molecules are electrons, as they have a mass of from one- to two-thousandth of the mass of an atom of hydrogen*.

2. In these experiments ultra-violet light was used as the ionizing agent and, as in the earlier experiments†, it was found that the current produced could be represented by the equation

$$n = n_0 \frac{(\alpha - \beta) e^{(\alpha - \beta)\alpha}}{\alpha - \beta e^{(\alpha - \beta)}} \cdot \cdot \cdot \cdot \cdot \quad (1)$$

when both positive and negative ions were actively engaged in the production of new ions by collision. Whilst, in weaker fields, before the positive ions have acquired sufficient velocity to be effective in this direction, the equation for the current becomes

$$n = n_0 e^{a\alpha} \cdot \cdot \cdot \cdot \cdot \quad (2)$$

Equation (2) proves sufficient for work up to $\frac{X}{p} = 15$ for argon, 30 for hydrogen, and the neighbourhood of 100 for nitrogen.

The usual nomenclature of the collision-theory is adopted without further explanation; and all symbols usually employed are retained in their usual form and with their usual meaning.

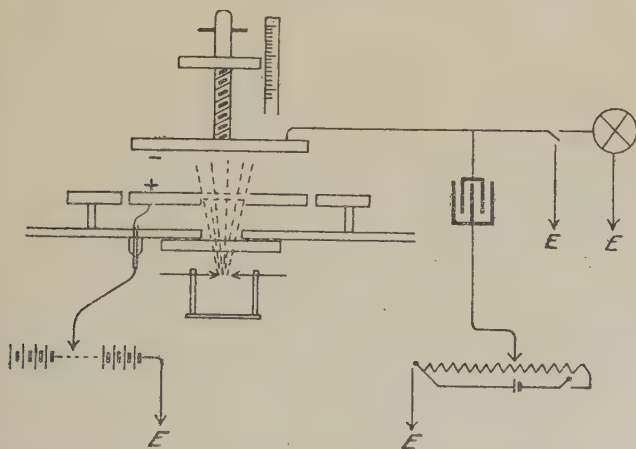
* J. S. Townsend and H. T. Tizard, Proc. Roy. Soc. A. lxxxviii. p. 336 (1913).

† Townsend, 'Electricity in Gases,' Chaps. VIII. to X.

3. The apparatus consisted essentially of a pair of well-insulated parallel-plate electrodes of silver, with guard-ring, in an exhaustible glass bell-jar. The centre part of the lower plate was pierced with parallel slits, in order to form a grid allowing of the admission of ultra-violet light from below to the ionization-chamber. The distance between the plates was accurately adjustable by a micrometer-screw worked from outside through a well-fitting socket. The slits in the lower plate were about $\frac{1}{7}$ of a millimetre wide, 1.5 cm. long, and 1 mm. apart. The diameter of the upper movable plate was 6 cm., and the maximum distance between the plates 1 cm.

The general arrangement of the apparatus is shown by the diagram in fig. 1, which will sufficiently explain itself.

Fig. 1



In the earlier experiments the electrodes were usually made of zinc, but it was considered desirable to use silver in these experiments to see if the determinations were affected by changing the metal of the electrodes. The recent experiments of Townsend and Bailey on the motion of electrons in argon showed that that gas is extremely sensitive to small quantities of impurities, and they found it advantageous to construct their apparatus, using glass instead of ebonite as an insulator.

The same precautions were taken in the apparatus used in these experiments, all electric insulation being effected by means of glass supports.

The contact of sealing-wax and grease with the gas

was reduced to a minimum by having ground-glass joints with the wax outside, wherever a fused glass joint was impossible. The electric leads were admitted through capillary tubes which fitted into carefully ground sockets, and the wires were sealed into these only in the outer half of the tube.

The object of these precautions—prevention of contamination of the gas—appears to have been fairly successfully attained, if one judges by the steadiness of the gas-pressure and the uniformity of the observations in the case of the hydrogen and nitrogen.

The currents were measured by the Induction Balance method* generally used in these experiments, and all wires, the electrometer, condensers, and glass jar were well screened.

4. The gases were prepared by the following methods:—

Hydrogen. A palladium tube was fused into the glass tubing of the apparatus and surrounded by an exhaustible silica sleeve. This sleeve was attached to a voltameter for the production of the gas by the electrolysis of barium hydrate, and pure hydrogen was admitted to the apparatus through the palladium by applying heat outside the sleeve.

Nitrogen. This gas was produced chemically by very slightly warming a mixture of equal parts of sodium nitrite, ammonium chloride, and potassium bichromate in three parts of water. The gas was then passed successively over KHO , H_2SO_4 , and heated metallic copper.

In each case the gas was stored in a flask over P_2O_5 and allowed to stand for at least a week.

Argon. The gas used in these experiments was a specimen of that which had been carefully purified for the experiments on the velocities of electrons referred to above, and the results of those experiments show that impurities probably amounted to less than .01 per cent. A flask containing the specimen of pure argon was sealed to the apparatus, and the gas admitted by means of a mercury-sealed tap.

5. After repeatedly exhausting and washing out the apparatus with pure gas, the ionization experiments were carried out with gas-pressures ranging up to about 100 mm., and electrode-distance up to its full amount whenever possible.

* J. S. Townsend, *Phil. Mag.* (6) vi. p. 598 (Nov. 1903).

6. These experiments were made over large ranges of electric forces and gas-pressures, in order to compare the results with those of the earlier investigations. It will be seen that the present results are in good agreement with the earlier ones in hydrogen and nitrogen; but in the case of argon the agreement was not good in the determinations corresponding to the lower values of the ratio $\frac{X}{p}$.

7. The ratios $\frac{\alpha}{p}$ and $\frac{\beta}{p}$ corresponding to different values of $\frac{X}{p}$ are shown in Tables I., II., and III. The distance S , at which sparking should occur, calculated from the equation

$$\alpha - \beta e^{(\alpha - \beta)S} = 0,$$

affords a means of comparing the sparking-potential V , obtained experimentally, with the calculated sparking-potential XS .

Tables I. to III., and the curves in figs. 2, 3, 4, 6, and 7, give a general survey of the results obtained; whilst the results obtained with the lower values of $\frac{X}{p}$ are represented on a larger scale in the remaining figures.

8. In order to detect any leakage of air into the apparatus tests were regularly made, each of several days' duration, after each series of observations. The apparatus was completely exhausted and the McLeod gauge watched. The leakage was always so small as to be negligible, when it is remembered that the gas was rarely more than a few hours in use. After that it was always pumped out into the air, and fresh gas taken for the next series of observations.

9. Special reference, however, must be made to the effect of impurities upon the behaviour of argon.

When this gas was examined by Gill and Pidduck, their specimen was probably not of the highest purity. There was a leakage in the apparatus of .01 mm. per day, but they found it did not appreciably alter the electrical properties of the gas.

It will be seen from the results of the present investigation

that a very small quantity of impurities affects the electrical properties of pure argon, but that there is no similar effect in pure hydrogen or nitrogen.

Gill and Pidduck also made experiments with helium* which showed that its electrical properties were much affected by impurities, and, in consequence, a second investigation was made with much more carefully purified gas. The difference in the results was remarkable, and bears a very strong resemblance both in nature and magnitude to the difference between very pure and slightly impure argon observed in the present investigation.

During the period of the experiments with argon, the leakage tests referred to in the preceding section never showed a greater rate of leakage than $\frac{1}{40}$ mm. in five weeks (*i. e.* less than $\frac{1}{1500}$ mm. per day). The contamination due to this during the period of two hours, over which determinations generally extended, must therefore have been quite negligible.

In these first few hours, however, measurable changes in the electrical properties of argon were found to take place on each occasion.

It seems probable that the cause of these changes was the vaseline-lubricant used in the air-tight socket through which the micrometer of the present apparatus was worked. This explanation is strengthened by the fact that Townsend and Bailey, although using a distinctly more sensitive apparatus in their recent work with argon, found a considerably less tendency in pure argon to change in the first few hours. Their apparatus was free from the above-mentioned possible source of contamination.

10. Under these circumstances, speed of measurement was essential; and it was found possible, by working at three definite distances (3, 6, and 9 mm.) between the electrodes, to take quite a large number of readings within an hour of the entry of the gas to the ionization-chamber.

If the gas was retained in the chamber for a few days the values of α and β became stationary, and after five weeks no further changes were observed.

11. The experiments for the pure and the slightly impure gas were made over the whole range of forces and pressures

* E. W. B. Gill and F. B. Pidduck, *Phil. Mag.* xvi. pp. 280-290 (Aug. 1908), and xxiii. pp. 837-848 (May 1912).

corresponding to $\left(\frac{X}{p} = \right) 0.8$ to 600; and it was found that above 200 the $\frac{\alpha}{p}$ values differed very little from those of the earlier investigators.

The $\frac{\beta}{p}$ factor for the positive ions was, however, always much higher than theirs—a fact which is confirmed by the low sparking-potentials which were obtained in these experiments.

Of necessity, during any series of readings, close approach to the sparking-potential had to be rigidly avoided. Economical usage of the gas also required that the observations of sparking-potentials should, in general, only be taken after using the gas for an hour or so. A few sparking-potentials were, however, taken with pure gas fresh from the storage flask.

12. The mean results of the determinations for hydrogen and nitrogen are given in the following tables:—

TABLE I.
Hydrogen.

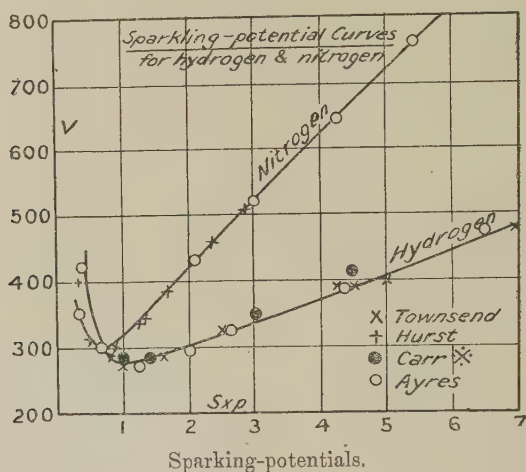
$\frac{X}{p}$	$\frac{\alpha}{p}$	$\frac{\beta}{p}$	$S \times p$	X.S.	V.
5	0060				
10	0105				
15	0177				
20	0243				
25	0367				
30	0726	00015			
40	194	00065			
50	354	0016			
60	560	0030	9.40	564	570
80	970	0068	5.15	412	412
100	1370	0116	3.50	350	351
125	1800	0215	2.50	313	315
150	2.12	0365	1.96	294	294
175	2.41	0560	1.61	282	283
200	2.63	079	1.38	277	277
300	3.30	200	.91	273	272
400	3.65	325	.73	292	291
500	3.92	455	.63	315	313
750	4.32	.74	.49	367	363
1000	4.60	.92	.44	438	420
2000	4.88	1.30			
3000	4.95	1.47			

TABLE II.
Nitrogen.

$\frac{X}{p}$	$\frac{\alpha}{p}$	$\frac{\beta}{p}$	$S \times p$	X.S.	V.
5					
10	011				
15	0170				
20	0239				
25	0305				
30	0382				
40	0550				
50	0820				
60	121				
80	257	0000			
100	471	0002			
125	850	0013	7.65	956	965
150	1.32	0048	4.27	641	648
175	1.84	0084	2.95	516	518
200	2.50	013	2.12	424	425
300	4.10	058	1.06	318	318
400	5.43	103	.75	300	298
500	6.29	157	.60	300	302
750	7.91	301	.43	323	322
1000	9.02	422	.36	357	350
2000	11.24	683			
3000	12.10	804			

13. The results of the experiments are shown by the curves in figs. 2, 3, and 4. The points marked in the diagrams give the results of the earlier investigators.

Fig. 2.



* W. R. Carr, Phil. Trans. A. cci. p. 403 (1903).

Fig. 3.

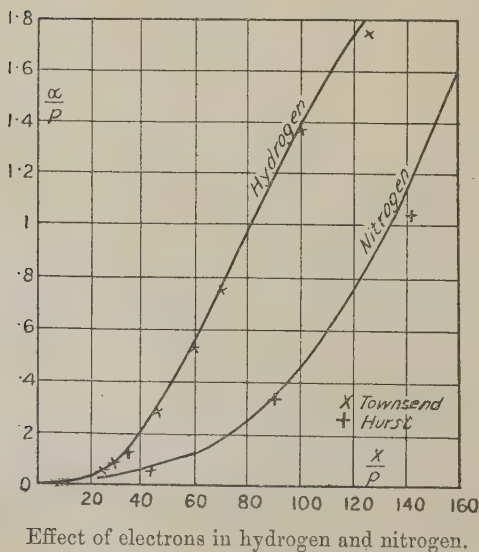
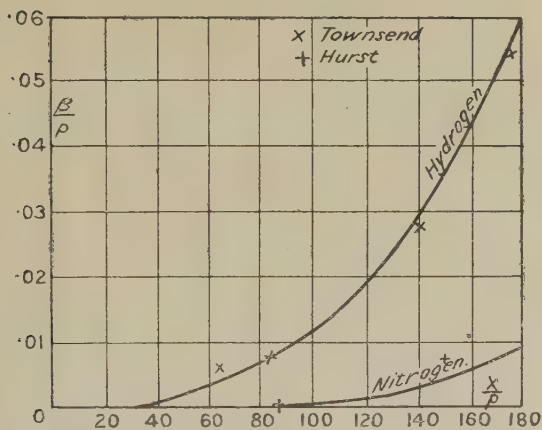
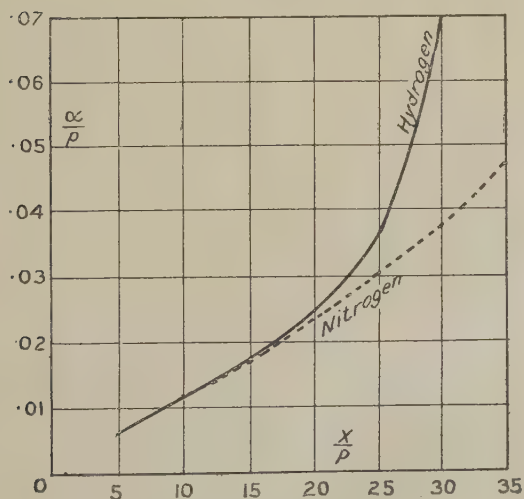


Fig. 4.



Effect of positive ions in hydrogen and nitrogen.

Fig. 5.



Effect of electrons in hydrogen and nitrogen.
(Enlarged scale.)

It is desirable to emphasize the fact, that, although the observations represented in the foregoing figures are expressed as the ratios $\frac{X}{p}$, $\frac{\alpha}{p}$, $\frac{\beta}{p}$, yet each particular value found was

the result of a number of different observations (generally about 10) at pressures as diverse as possible. The ratios so obtained were approximately equal, and it is their mean values which are finally given in this paper.

14. Table III. shows the results obtained for Argon on the same plan as the previous tables.

TABLE III.
Argon (pure).

$\frac{X}{p}$	$\frac{\alpha}{p}$	$\frac{\beta}{p}$	$S \times p$	$XS_{(calc.)}$	V.
2	·005				
5	·075				
10	·182	·0000			
15	·300	·00067			
20	·440	·00164	12·8	256	
25	·550	·00278	9·87	247	
30	·700	·0039	7·52	226	218
40	·960	·0064	5·25	210	208
50	1·22	·0089	4·08	204	203
60	1·48	·0114	3·32	199	200
70	1·738	·0140	2·80	196	197
80	1·976	·0167	2·44	195	195
90	2·220	·0195	2·16	194	194
100	2·45	·0223	1·94	194	194
125	3·02	·0290	1·552	194	193
150	3·567	·0371	1·295	194	193·5
175	4·11	·0450	1·111	194	194
200	4·64	·0546	·970	194	194
300	6·40	·100	·661	198	198
400	7·80	·160	·511	204	(205)
500	8·70	·235	·428	212	(211)
600	9·35	·330	·374	220	(225)

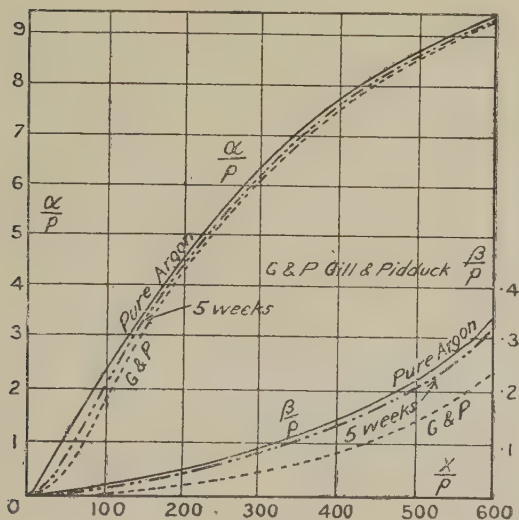
TABLE IV.
(Argon).

	p	S	$S \times p$	V.
(a)	·97	1·0	·97	194
	2·10	1·0	2·1	194
	5·2	1·0	5·2	210
(b)	·41	1·0	·4	207
	2·08	·5	1·04	200
	2·08	·8	1·66	198
	2·08	1·0	2·08	202
	5·21	·6	3·12	210
	5·21	1·0	5·21	224
	9·00	·7	6·3	226
	9·00	·9	8·1	234
	9·00	1·0	9·0	232
	15·0	·8	12·0	242

The actual sparking-potentials found experimentally in Argon are shown in Table IV. (a) with pure gas just admitted to the ionization-chamber ; (b) with gas which had been in use for about an hour in ionization experiments.

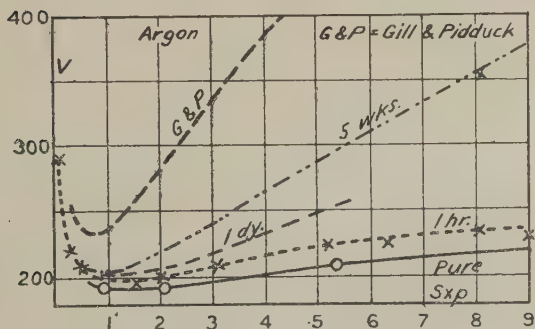
15. The numerical results given in the preceding tables for Argon are represented graphically in the following figures :—

Fig. 6.



The continuous curve represents results obtained with pure Argon. The lower dotted curve gives the results obtained by Gill and Pidduck, whilst the intermediate curve shows values of the ratios after the gas had stood in the ionization-chamber for 5 weeks.

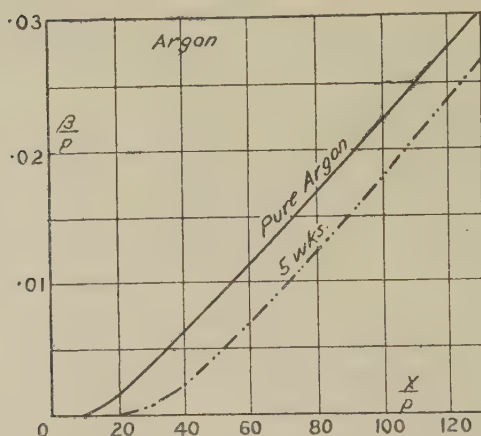
Fig. 7.



Sparking-potentials.

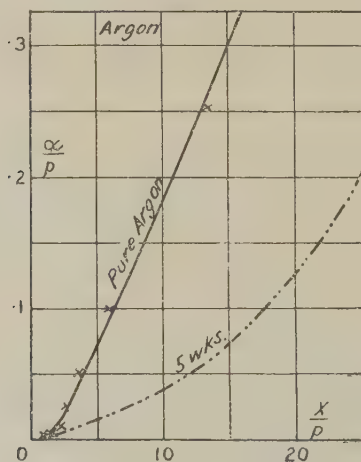
The change in the sparking-potential due to impurities was more rapidly evident than in other measurements. Fig. 7 shows by a continuous curve determinations obtained with the pure gas. The intermediate dotted curves indicate the effect of very slight impurities at certain approximate intervals of time up to 5 weeks.

Fig. 8.



Effect of positive ions in pure Argon and in Argon which was slightly impure.

Fig. 9.



Effect of electrons in Argon. (Enlarged scale.)

16. For certain gas-problems information given in the ratio form of Tables I., II., and III. is insufficient. Consequently, for the purpose of supplying exact data as regards the actual pressure, distance between electrodes, maximum voltage, &c., a number of actual examples from each gas are tabulated in the order of the ratio $\frac{\chi}{p}$ in Table V.

TABLE V.

Argon.

$\frac{X}{p}$	X.	p.	a.	v.	α .	β .	t.
1.05	63	60	.9	56.7	.063	—	10
2.14	34.2	16	.9	30.8	.132	—	15
2.56	41	16	.9	36.9	.389	—	20
3.50	55.9	16	.9	50.3	.817	—	5
5.95	95.1	16	.9	85.6	1.523	—	10
13.4	69.4	5.21	.9	62.5	1.303	—	5
33.3	173.3	5.21	.9	156	3.527	.0266	60
40.0	208	5.21	.9	187	5.05	.0355	0
40.0	208	5.21	.9	187	4.63	.0303	60
* 74.6	190	2.55	.8	152	4.74	.0389	10
97.5	248.5	2.55	.8	196.5	5.142	.0415	10 dys
192	252.4	1.325	.7	176.7	5.762	.0620	60
349	292	.838	.6	174.5	5.87	.108	33 dys
507	323	.638	.6	194	5.67	.167	15
* 613	229	.374	.8	183.2	3.52	.119	33 dys
* 621	396	.638	.5	198	6.02	.220	30

Hydrogen.

5.15	51	9.9	1.0	51	.063	—
10.3	102.5	9.9	1.0	102.5	.105	—
26.0	204	7.85	1.0	204	.311	—
* 50.3	206	4.1	1.0	206	1.515	.0053
73.6	301.5	4.1	1.0	301.5	2.42	.023
124.2	122	.985	1.0	122	1.720	.0203

Nitrogen.

9.7	112	11.5	1.0	112	.128	—
24.8	61.5	2.48	1.0	61.5	.075	—
61	915	15	.5	458	1.91	—
* 165.2	410	2.48	.9	369	4.13	.0176

A few examples are then given illustrating the degree of closeness of the theoretically calculated currents [using equations (1) or (2)] to the currents measured experimentally.

The symbols employed have the following meaning :

X = field-strength in volts per cm.

p = gas-pressure in mm.

a = distance apart of electrodes in cm.

v = maximum voltage difference employed.

$e = e^{\alpha a}$.

$$E = \frac{(\alpha - \beta) \epsilon^{(\alpha - \beta)a}}{\alpha - \beta \epsilon^{(\alpha - \beta)a}}.$$

α, β = the number of pairs of ions produced per cm., by collision, by one negative or one positive ion respectively.

t = time in minutes after first admission of gas to chamber.

q = the current observed (in arbitrary units).

17. Of the following examples those marked (*) are taken from the preceding table.

Argon.

(Pure Argon.)

*	$a.$.2.	.4.	.6.	.8.
q	22	58.5	161	550	
e	22	56.8	146	376	
E	22	58.3	163	550	

$X=190.$ $p=2.55.$ $\alpha=4.74.$
 $\beta=.0389.$

(Gas which has been in ionization-chamber one week.)

	$a.$.2.	.4.	.6.	.8.	1.0.
q	12.5	28.2	69.0	180	600	
e	12.5	28.2	63.1	142	319	
E	12.5	28.5	68.0	178	599	

$X=204.$ $p=2.55.$ $\alpha=4.05.$
 $\beta=.0363.$

(Pure Argon.)

*	$a.$.1.	.2.	.3.	.4.	.5.
q	19.7	37.5	74	171	565	
e	19.7	35.9	66.3	120	219	
E	19.7	37.1	73.9	169	566	

$X=396.$ $p=.638.$ $\alpha=6.02.$
 $\beta=.220.$

(Gas which has stood 5 weeks.)

*	$a.$.1.	.2.	.6.	.8.
q	18	25.5	126	380	
e	18	25.8	105	212	
E	18	25.9	127	380	

$X=229.$ $p=.374.$ $\alpha=3.52.$
 $\beta=.119.$

Hydrogen.

*	$a.$.2.	.4.	.8.	1.0.
q	8.4	16.7	69	158	
e	8.4	16.7	65.3	130	
E	8.4	16.8	70.7	158	

$X=301.5.$ $p=4.1.$ $\alpha=2.42.$
 $\beta=.023.$

Nitrogen.

*	$a.$.1.	.5.	.7.	.9.
q	13	64	161	420	
e	13	66	153	349	
E	13	67	159	420	

$X=410.$ $p=2.48.$ $\alpha=4.13.$
 $\beta=.0176.$

18. The following is a short summary of results obtained:—

I. *With Hydrogen and Nitrogen:*

1. The values obtained for both $\frac{\alpha}{p}$ and $\frac{\beta}{p}$ are in good agreement with those found by Townsend and Hurst.

2. For nitrogen, however, values of $\frac{\alpha}{p}$ are slightly higher than Hurst's in the range $\left(\frac{X}{p}\right) = 100$ to 350; whilst in the same range $\frac{\beta}{p}$ values are lower than his.

3. The effect of the electrons was observed for values of $\frac{X}{p}$ as low as 5 in hydrogen and 10 in nitrogen.

4. The effect of the positive ions was observed for values of $\frac{X}{p}$ as low as 30 for hydrogen, and 100 for nitrogen.

5. No evidence was obtained of any distinctive variation in the ionization due to *slight* contamination of these gases. The effect due to *larger* amounts of impurities has already been inquired into by the earlier investigators.

6. As the earlier work was done with brass and zinc electrodes, and the present with silver electrodes, the nature of the metal used seems to have no appreciable effect on the processes by which the currents increase with the distance between the plates.

II. *With Argon:*

1. There is a general agreement between the values of $\frac{\alpha}{p}$ and $\frac{\beta}{p}$ corresponding to the higher values of $\frac{X}{p}$ obtained in these experiments and those found by the earlier investigators.

2. The values of $\frac{\alpha}{p}$ and $\frac{\beta}{p}$ corresponding to the lower values of $\frac{X}{p}$ were larger than those previously obtained.

3. The effect of the electrons was observed for very small values of the ratio $\frac{X}{p}$, as low as 2.

4. The effect of the positive ions was measurable with pure gas down to $\frac{X}{p} = 10$; but with slight contamination it was not detected lower than $\frac{X}{p} = 20$.

5. In the region $\left(\frac{X}{p}\right) = 2$ to 10, the effect of the electrons may easily be reduced by impurities to one-fifth of its value with pure argon.

6. Comparatively low sparking-potentials were obtained, and it was found that impurities increased the sparking-potential.

19. I wish in conclusion to thank Professor Townsend, both for the specimen of carefully purified argon which he kindly supplied to me, and also for his constant sympathy and ready advice on all occasions.

XXXVII. *On certain Fundamental Principles of Scientific Inquiry. (Second Paper.)* By DOROTHY WRINCH, D.Sc., Fellow of Girton College and Member of the Research Staff, University College, London, and HAROLD JEFFREYS, M.A., D.Sc., Fellow of St. John's College, Cambridge*.

IT is a universal belief among physicists that when a sufficient number of inferences from a quantitative law have been verified, the probability of the correctness of the next inference from it may be made to approach indefinitely near to unity. It was shown in a former paper † that this proposition is not easily reconcilable with the other proposition, also believed by some physicists, that all laws of some infinite class are equally probable *à priori*; but that it is a necessary consequence of the contradictory proposition, which appears not unplausible, that the prior probabilities of admissible laws are not all equal, the simpler in fact having the higher probabilities. It was pointed out further that, if the admissible laws are all arranged in a series according to their probabilities, the current process of taking the simplest law that fits the facts can never enable one to proceed more than a finite number of steps along this series, and accordingly the laws capable of being discovered must form an

* Communicated by the Authors.

† Phil. Mag. xlii. pp. 369-390 (1921).

enumerable aggregate. In particular, since it appears that the constants in physical equations are often capable of continuous variation, or of discontinuous variation through more values than can be examined, we must suppose that laws containing such parameters are not in forms suitable for the comparison of their probabilities. They must have these parameters removed, by differentiation or otherwise, before such a comparison can be carried out. In particular, where a law can be expressed as a differential equation or as its integral, the latter involving one or more arbitrary constants, the latter cannot be the fundamental form of the law in our knowledge, while the differential equation may be. One consequence of the inadmissibility of quantities capable of discontinuous variation through more than a certain number of values is that the fundamental form of the law of gravitation cannot involve the mass of the attracting body explicitly. Thus the Newtonian form of it cannot be the fundamental one; nor can the Poisson form nor the equation in Einstein's system that corresponds to it, since the density occurs as a parameter in these and is capable of many values. On the other hand, the Laplace equation holding in regions containing no matter, or the corresponding Einstein equation

$$G_{\mu\nu}=0,$$

may be fundamental. This appears to be the decisive and unequivocal answer to the question, whether action takes place at a distance or by continuous transference: there is no question as to the truth or otherwise of the differential as against the integrated forms of the law of gravitation, since they in fact imply each other; but the differential form is more fundamental in knowledge since it sums up all possible forms of the integrated law. Again, the non-fundamental character of Poisson's equation and its analogue seems to require the density itself to satisfy a definite differential equation, which scarcely seems possible in view of the way we can vary it at will, or else that these equations are only macroscopic in character. The latter alternative would require that Laplace's equation or its analogue holds strictly at all points not within the ultimate particles of matter, and that the arbitrariness in the solution is supplied by the boundary conditions at the margins of these.

It was pointed out in the paper already referred to that laws differing slightly with regard to some fundamental constant must be in general widely separated in the series arranged

according to prior probabilities. If, for instance, the law involves only two terms, and in one possible law the constant considered is an integer, while in the other it differs from this integer by $1/n$, we showed that in one plausible arrangement these laws would be separated by something of the order of $\pi(n)$ terms, where π^* is the number of numbers less than n and prime to it.

It follows that the law established with a high probability by experience is never an approximation to the simple law, but the exact simple law itself. In other words, extrapolation over an indefinitely wide range can be carried out with the full probability of the law. This statement, however, requires further discussion. The data actually obtained by experiment are never such that they can *exactly* satisfy a quantitative law as they stand; they are of the form "the mark x lies between the n th and $(n+1)$ th marks on the scale" or "the sensation y occurred between the m th and $(m+1)$ th ticks of the clock after the last minute." There are two possible attitudes towards such measures. We can say either that they form a series of discrete values like n and m , only a few of which can possibly satisfy the law exactly; or that there is in each case a "true value" to which the measured value is only a rough approximation, and which does accurately satisfy the law. The latter alternative appears plausible at a first view, but is quite inadmissible as a part of knowledge. In the first place, as has been stated above, many of the quantities are involved through their differential coefficients, which are in no case directly measurable. Further, if it be once admitted that there is a true value which may be equal to any value in a certain compact series, so far as our prior knowledge can tell us, we must recognize that the number of possible true values that fit the law is infinite; for if the law connects x and y , say, there will be certain ranges of values of x and y such that every value of x within one corresponds to a value of y within the other, and *vice versa*. Thus the "true value" can in no case be determined uniquely from the knowledge at our disposal.

The solution of the difficulty appears to rest in a definite admission that the observations in fact do not as a rule satisfy the law. The fundamental data of all empirical knowledge

* It has been proved that $\pi(n)$ is asymptotically equivalent to $n/\log n$. For other properties of this function $\pi(n)$ reference should be made to the writings of Mertens, Hadamard, Von Mangoldt, De la Vallée-Poussin, Landau, Littlewood, and Hardy. References may be found in Landau's *Primzahlen* (Teubner, 1909).

are sensations ; those sensations involved in measurement form a large class of special interest for physics. The laws of physics are derived from measures, with the assistance of certain other principles of a non-logical character, the principle of simplicity being among the chief. They are therefore less fundamental in knowledge than the data of measurement.

Any observed measure is liable to differ slightly from the measure of the same quantity calculated by inference from the laws established. This is a matter of experimental fact ; and it is no violation of our principles that it should be so, for it is characteristic of quantitative inference that it only infers an observed value approximately and with a high degree of probability. It does infer that the observed value will lie within certain limits ; these are to be found as follows. If any measured quantity l_r is found to lie between n_r and $n_r + 1$ units, and another measure l_s is to be inferred from a number of such measures, we obtain the maximum limit by supposing each measure l_r to have the value n_r or $n_r + 1$ units, whichever gives the greater calculated value of the measure l_s to be inferred. By an analogous procedure we can find the lower limit of the inferred quantity, and our inference is strictly of the form that the observed measure will almost certainly lie within the limits thus obtained. In our subsequent work we shall not usually state our results in this form, but in the more compact one given by the simple law itself. Nevertheless, they can always be restated in the strict form by applying the above rules, and it is only when this has been done that verification has any meaning.

Inferences of this form are all that are ever made in science, and the characteristic feature, namely, a certain latitude in the verification, which we by convention call the margin of error, duly appears in the result. It follows by the argument in our former paper that if the law has a finite prior probability, we can by making a sufficient number of verifications make the probability of subsequent verifications approach indefinitely near to unity. Accordingly, this postulate is a sufficient explanation of the high probability usually attached to quantitative inference.

As has already been stated, it would be an error to consider that this result proves that scientific inference has a wholly logical basis. The theory we have developed links together a postulate which has been stated in formal terms *

* *Loc. cit.* pp. 378-9.

in the paper already quoted, and is summarized in the opening paragraph of the present paper, with the proposition, habitually assumed in science, that quantitative inference from the simplest law that fits the facts is reliable. It is, indeed, proved that the second is a logical consequence of the first. The denial of the first would make it extremely difficult to construct a theory that would include the second. The result therefore constitutes a contribution to scientific methodology, which aims at reducing the propositions habitually assumed in scientific investigations to groups of more fundamental propositions which imply them, and is not an attempt to prove that these fundamental propositions have themselves a basis in logic. The sole reasons for believing them are their intrinsic plausibility and the unplausibility of consequences deduced from their contradictions.

The structure of the theory of scientific method is strictly analogous to the structure of pure geometry, each consisting of a set of fundamental propositions with a logical superstructure. The main differences are that the fundamental propositions of science include facts of sensation, and that principles of probability inference, including empirical generalization, are employed in the development. Given all the fundamental propositions of scientific inference, the probability of any proposition whatever in science is determinate.

In practice, one is not interested only in the relation between the fundamental propositions and the inferences from them; for it is important to be in a position to assert the inferences without repeating the fundamental propositions every time. This will be accomplished only if the fundamental propositions are believed. We have indicated reasons for believing them, but we must repeat that this belief is at bottom not logical. The theory we are attempting to construct is one that includes the processes actually employed by scientific workers; since psychology is by definition the study of behaviour, this work may perhaps be regarded as a part of psychology. We think that the use of such a theory is to facilitate the understanding of the structure of physics, and thereby to suggest which methods of development and criticism are in closest accordance with the principles that are generally believed to lead to reliable results. For instance, one often hears the legitimacy of inference criticised in the case of new and unfamiliar laws, and it seems desirable that it should be pointed out that the

process of inference and the reason for believing the results are just the same in these cases as with laws that have been known much longer.

In addition to the known measured value of a physical quantity and the unknowable "true value" there may be a third quantity not found wholly by measure, and quite unique. This we shall call the "adopted value." This occurs when we have a number of observations of one or more variables, which have been found to be fitted approximately by one or more physical laws. The case of a single measurement carried out several times may be included under this head, the law involved being merely one of constancy with regard to the time. The observations will not in general fit the law exactly, and it may be useful to adopt some method of finding values near to them that do fit it exactly. The Method of Least Squares is one specially convenient method, but there are many others. It is a matter of convention which method we adopt, but when we have chosen one the values found by it are unique. These values are called the adopted values. They are evidently less fundamental in knowledge than the laws, and still less so than the measured values.

We have remarked already that the measurable values of a quantity form a discrete series containing an enumerable set of terms; hence its ordinal type is finite or ω . Irrational numbers form no part of the measurable values. On the other hand, the adopted values form a compact series. For, suppose a quantity to be measurable as either n or $n+1$ units. Then it is possible that after a number of measures have been made, r of them have been found equal to n and s to $n+1$. The adopted value, according to the usual least square method, would be $n + \frac{s}{r+s}$. Now, however short the interval between two numbers both less than 1 may be, there are always values of r and s such that $s/(r+s)$ lies between them. Hence there are possible adopted values of the quantity in every interval from n to $n+1$, and in general we may say that the possible adopted values form a compact series. On the other hand, the cardinal number of this series is only \aleph_0 . For, the possible physical laws have number \aleph_0 . Each has a finite number of integrals. These, with any conventional method of fitting, give in each case a single finite set or a finite number of finite sets of adopted values. Hence, by the method used to show that

the roots of all algebraic equations are of number \aleph_0 , we may show that the possible adopted values have number \aleph_0 . Hence the possible adopted values of any variable form a series of ordinal type η .

It is often desirable to express physical laws in forms involving only ratios of measures among themselves, and not a specified unit. An example of this procedure is to be found in the fundamental result used in our forthcoming development of mensuration. Each such ratio is the ratio of two terms, each of which may have any integral value in terms of the unit; hence the possible values of such ratios form a series of ordinal type η , the type of the rational fractions in order of magnitude. The special advantage of this method of expressing a law is, of course, that it remains completely unaltered when a change of units is made.

On the other hand, any continuum must have number 2^{\aleph_0} . This introduces a theoretical difficulty. For it follows from the foregoing argument that no physical law in its integrated form can involve variables capable of more than \aleph_0 values, even if we include adopted values and ratios of measures. Hence continua have no place in physics; the closest type of series possible is η .

The ordinary discussions of differentiation cover cases of the differentiation of functions specified for all values of a continuous variable. Such specification, as we have already shown, is never possible in physics. It is sufficient for our purposes, however, to define differentiation in such a way that it can be applied to functions specified for only an η of values. In the case of functions specified only for a finite number of discrete values, the differential coefficients must be defined by the conventional process of interpolation; this is, indeed, how they are always found in practice.

XXXVIII. *The Calculation of the Magnetron Number of an Atom in Solution.* By J. H. SMITH, M.Sc., Assistant in Physics, University College, London*.

WEISS (*Le Radium* p. 8, 1911), using the numerical results of a large number of experimental measurements of the magnetic susceptibility of metals of the iron group and of their compounds, concluded that the magnetic moment of an atom of this group was always an integral multiple of an ultimate magnetic unit which he called the magneton.

The magnetic moment per gram molecule of a substance at absolute zero is calculated in the following way.

Let χ be the volume susceptibility at a temperature T° Abs. of a substance of density d and molecular weight M . The molecular susceptibility at T° is $M \frac{\chi}{d}$. Using Langevin's theory for a paramagnetic gas we have $\frac{I}{I_0} = \frac{I_0 H}{3RT}$, where I and I_0 are intensities of magnetization, H the external magnetic field in absolute C.G.S. units, and R is the gas constant 8.315×10^7 ergs.

The magnetic moment per gram molecule at absolute zero

$$= \sqrt{3RTM \frac{\chi}{d}}.$$

In the case of solution the theory of Langevin for a paramagnetic gas is assumed to hold good. In general also Wiedemann's law that the magnetic susceptibilities are purely additive is also assumed. For solution of the chlorides, nitrates, and sulphates of the iron group in water, this has been verified by several workers. (A review of published work on the theory is given by Cabrera, *Journal de Chimie Physique*, xvi. 1918.)

The magnetic moment per gram atom for the metal is found by subtracting the diamagnetic moment per gram acid radicle (*i. e.* for Cl_2 , SO_4 , or NO_3) from the magnetic moment of the gram molecule found as above. The values of the diamagnetic moments of the acid radicles are taken from those deduced by Pascal (*Annales de Chimie et Physique*, xix. 1910) from measurements of magnetic susceptibility for series of organic compounds. These values are corrected to agree with the later determinations of the susceptibility of water, since Pascal made all his measurements using water

* Communicated by Prof. A. W. Porter, F.R.S.

as a standard. The accepted value was then $\cdot 75 \times 10^{-7}$; $\cdot 720 \times 10^{-7}$ is the mean value of the most recent determinations.

The magnitude of this correction is shown in the following example taken from the results of Weiss and Bruins (*Koninklijke Akademie van Wetenschappen te Amsterdam*, xviii. p. 1, 1915):—

Molecular susceptibility of nickel chloride $443\cdot6 \times 10^{-5}$

Atomic susceptibility of nickel at 18° C. $447\cdot6 \times 10^{-5}$

The correction for the Cl_2 radicle, $4\cdot0 \times 10^{-5}$, is seen to be about 1 per cent. For cobalt and iron salts the percentage correction is rather less.

In addition to so allowing for the Cl radicle there is a further correction of the same type which ought to be made; for in the molecule of nickel chloride there must be two systems with diamagnetic moments. The nickel atom itself must have a diamagnetic moment which is comparable with that of the Cl_2 radicle.

The typical atom of the iron group must consist of a nucleus and planetary system, in which the orbits of the outer electrons are mutually compensatory as regards the magnetic field produced by them at any external point, with the addition, characteristic of the group, of an uncompensated orbit. By an uncompensated orbit is meant one which can be rotated by external magnetic fields.

Let A be the centre of the uncompensated element of such an atom. Any other single electron in the atom, moving in a circular orbit with frequency n , will produce a magnetic field for which the magnetic vector at A can be written Gne —where G depends on the size of the orbit and the position of A with regard to it. Suppose that μ is the magnetic moment of the uncompensated element. Between the latter and the orbit considered there will be a relative magnetic energy $Gne\mu \cos \phi$, where ϕ is the angle between the axis of μ and the vector Gne . If $\sum Gne \cos \phi \mu$ be taken for all the orbits of the atom, the result will be zero if there is only one uncompensated orbit. But even if this is so, the orbits of the compensated type must have a diamagnetic moment which is comparable with that of the acid radicle. Thus all the values which have been calculated for the magnetic moments of the paramagnetic atoms must be smaller than the magnetic moment of the uncompensated element alone. The diamagnetic moment of the atom must also vary with the frequency of the electrons in compensated orbits, unless there is a change of area of orbit with frequency, such that the product of these two is constant.

Weiss and Bruins (*loc. cit.*) found that, when ammonia is added to solutions of nickel salts in water, the magneton number of nickel drops from 16.03 to 15.57, although Wiedemann's additive law is still obeyed. If the moment of the uncompensated orbit remains constant, then, on the addition of ammonia, there must be an increase in the diamagnetic moment of the nickel atom. The colour of the solution changes from green to brown, and this indicates a change of frequency of the electrons which are responsible for light-absorption. If measurements were made on the change of position of the absorption bands, characteristic of the nickel atom in solution, when the ammonia is added it might be possible to obtain some relation between the change of frequency and the increase of diamagnetic moment.

Since there was no apparatus available to investigate the colour change of the nickel solutions, it was decided to use instead cobalt chloride solutions in water and in absolute alcohol. The solutions of cobalt salts in water have a well-defined absorption maximum in the green, which moves towards the red end of the spectrum when the salts are dissolved in alcohol.

The positions of the maxima of these bands were investigated with a Hüfner spectrophotometer, as modified by Mees ('Photographic Journal,' July 1904).

In water solutions the absorption maximum was found to be at 0.510μ , and in the alcohol solutions at 0.65μ . These results are in good agreement with those obtained by Houstoun and Gray (Proc. R. S. Edinburgh, xxxi. p. 547), but differ from the positions estimated from series of photographs through solutions of different strengths by Jones and Anderson (Carnegie Publications 110).

The measurements of magnetic susceptibility were made with apparatus similar to that described by Pascal (*Annales de Chimie et Physique*, viii. p. 289, 1910). The method was first suggested by Kelvin. If the substance is obtained in the form of a uniform cylinder, and one end of the cylinder is situated in a field of strength H and the other end in a field of strength h , the cylinder experiences a force $\frac{1}{2}\chi(H^2 - h^2)S$, where S is the cross-section of the cylinder and χ is the apparent volume susceptibility of the substance, that is, the difference between its susceptibility and that of the surrounding medium. The force was measured by suspending a thin-walled glass tube containing the liquid from one arm of a balance, the base of the tube being situated between the poles of a large electromagnet, and finding the change in weight of the tube and contents when the current passes through the coils of the electromagnet.

The molecular susceptibility of the alcohol used was found, by comparison with water, to be 3.40×10^{-3} . The value found by Pascal (*loc. cit.*) was 3.43×10^{-3} , when corrected by the more recent value of the susceptibility of water.

The volume susceptibility of cobalt chloride in solutions of various strengths was found to be about 2 per cent. less in alcoholic solutions than in water solutions of the same strengths. The magneton number of cobalt in the water solutions, calculated by the method used by Weiss, was 24.6. Miss Brant ('Physical Review,' xvii. p. 678, 1921) found 24.5.

It is found therefore that, if the moment of the uncompensated element is constant, the diamagnetic moment of the molecule must increase, although the frequency of resonators corresponding to the absorption maximum is decreased. The areas of these orbits may change. It must also be remembered that they are probably only a part of the compensated system. A reasonable conclusion is that the frequency of the uncompensated element is diminished in the alcohol solutions, just as that of the light absorbers is diminished. The mass of evidence collected during recent years for the two paramagnetic gases (oxygen and nitrous oxide), for solutions, and for crystals shows that experimentally we find that neither the magneton of Weiss, nor that of Bohr, which is about five times the former, fits in with the experimental results.

The study of the variation of magnetic susceptibility with temperature in platinum and palladium has led Foëx (*Annales de Physique*, ix. p. 16, 1921) to conclude that these metals possess not only a diamagnetism which is independent of the temperature, but also a paramagnetic part to which he assigns the magneton number 8. It is evident that all atoms have a diamagnetic moment.

Westgren ('Journal of the Iron and Steel Institute,' May 1921) has shown that the crystal structure of iron does not change at the recalescence temperature, so that there can be considerable changes in the uncompensated orbits without any apparent change in the distribution of the outer electrons of the atom. A change in the distribution and frequency of the latter will, however, produce a change in the diamagnetic moment of the atom, as was shown by Oxley (*Phil. Trans. R. S.* 214. A. *et seq.*). Such changes account for the discontinuities observed by Theodoridès (*Comptes Rendus*, clxxi. p. 715, 1920), when he plotted $1/\chi$ against the absolute temperature for certain paramagnetic crystals.

FIG. 1.



Tracks in air. The α particles are not confined to a horizontal plane by means of a plate with a horizontal slit, as in the other photographs.

FIG. 2.



Tracks in air.

FIG. 3.



Tracks in Hydrogen, showing the α particles shooting completely across the chamber.

FIG. 4.



Tracks in Hydrogen, showing the α particles shooting completely across the chamber.

FIG. 5.



Tracks in Hydrogen, with aluminium foil interposed.

FIG. 6.



Tracks in Methane.

FIG. 7.



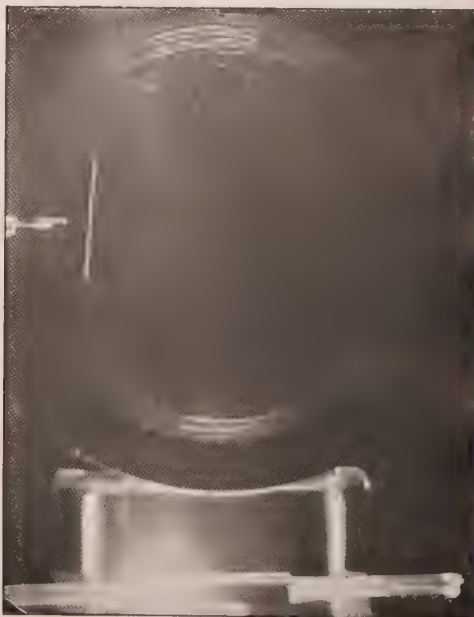
Tracks in Nitrogen.

FIG. 8.



Tracks in Carbon Monoxide.

FIG. 9.



Tracks in Oxygen.

FIG. 10.



Tracks in Carbon Dioxide.

XXXIX. *The Range of Alpha-Particles from Polonium in Various Gases.* By C. W. VAN DER MERWE, M.Sc.,
Lecturer in Physics, University of Cape Town*.

[Plate IV.]

THE Polonium which was the source of the α -rays in these experiments was kindly sent to me by Sir E. Rutherford through Mr. C. T. R. Wilson.

The range of the α -particles was determined by C. T. R. Wilson's† method of photographing the tracks in air saturated with water-vapour. Several improvements were made in the form of the apparatus. Wherever possible, brass was used in the construction instead of glass. A brass plate with a narrow horizontal slit, which was attached to the plunger, stopped the α -rays from traversing the cloud chamber, except at the end of the expansion when the slit was directly opposite the source of the α -rays.

Gelatine, which Wilson used for coating the inside of the cloud chamber, was found to be unsatisfactory because a fungus readily formed on it; but a jelly consisting of 6 parts by weight of glycerine (4 of water, 1 of gelatine, and 1 of sugar), proved satisfactory even at the higher temperature prevailing in Cape Town in the month of February.

Many photographs of the tracks in each gas were taken, and the maximum range on each plate was selected as being the range of the particle projected from the surface of the radioactive material in that particular experiment.

The initial temperatures and pressures were observed, and the final temperatures and pressures were calculated from the adiabatic expansion ratio.

The range in moist air was found to be 5.57 cm. at 258.1° K. and 462.2 mm. pressure, which corresponds to a range of 3.59 cm. at N.T.P. Geiger‡ found the range of α -particles from polonium by the ionization method to be 3.58 cm. at N.T.P., a highly satisfactory agreement between the two methods.

Since water-vapour is less dense than air, the range in

* Communicated by Sir W. H. Bragg, K.B.E., F.R.S.

† Wilson, Proc. Roy. Soc. A. lxxxv. p. 285 (1911).

‡ Geiger, Phil. Mag. Oct. 1911.

dry air should be less than that in air saturated with water-vapour; for, according to Sir W. H. Bragg *, the stopping-power of an atom is proportional to the square root of its atomic weight. An attempt was made to calculate the stopping-power of water-vapour relative to that of air from many determinations of the ranges in saturated air, assuming Geiger's value for dry air.

If m is the number of water-vapour molecules and n the number of air molecules, then the stopping-power of water-vapour is given by

$$\frac{ms+n}{m+n} = \frac{r_1}{r_2},$$

where r_1 is the range in dry air and r_2 is the range in moist air. Although these experiments gave a mean value of 0.77 as the stopping-power, while Bragg's formula gives 0.79, the method cannot be regarded as satisfactory for the purpose. The photographic tracks are faint near their ends, and therefore cannot be measured with the necessary accuracy, for r_2 is only slightly greater than r_1 . This faintness of the photographic tracks near their ends is explained by the experiments of Geiger † and G. H. Henderson ‡, who showed that the ionization along the path of the particle does not suddenly stop. The ionization goes on increasing slightly until near the end of the path, and then falls off very rapidly.

The experiments, however, show that we may assume the stopping-power of water-vapour equal to 0.79 in correcting for the presence of water-vapour in other gases.

The following table exhibits the stopping-powers of several gases determined in this way, alongside the values calculated from Bragg's law, as well as the values for rays from Radium A and Radium C determined by Bragg and Kleeman §.

The greatest difference between the experimental and calculated values of the stopping-power is that of hydrogen. This is explained by the fact that the range in hydrogen was too long for the cloud chamber, and it was cut down by interposing aluminium foil, whose equivalent hydrogen path

* Bragg, 'Studies in Radioactivity,' p. 42.

† Geiger, Proc. Roy. Soc. lxxxii, p. 489.

‡ Henderson, Phil. Mag. Oct. 1921, p. 538.

§ Bragg & Kleeman, Phil. Mag. x, p. 318 (1905).

had to be calculated. The calculated range of hydrogen is probably too large. Pl. IV. shows a few specimen photographs of the tracks.

Stopping-Powers.

	Source of α -rays. Polonium.		Bragg's Experiments.		Range at N.T.P.
	exp.	cal.	Radium A.	Radium C.	cms.
Air	1.00	1.00	1.00	1.00	3.58
Hydrogen	0.22	0.26	—	0.24	16.28
Water-vapour	0.77	0.79			
Methane	0.91	0.98	0.88	0.86	3.96
Nitrogen	0.99	0.99	0.98	0.99	3.62
Carbon Monoxide ...	1.02	0.98	0.98	0.99	3.51
Oxygen	1.08	1.06	1.057	1.064	3.32
Nitric Oxide	1.11	1.02			3.23
Carbon Dioxide	1.52	1.51	1.49	1.51	2.36
Sulphur Dioxide ...	1.82	1.80			1.97
Methyl Bromide ...	2.04	2.08	2.03	2.09	1.76

Summary.

An experimental determination of the ranges of α -particles from Polonium, in several gases, by Wilson's photographic method proves that the stopping-powers of these gases may be calculated from Bragg's law.

I wish to express my appreciation of the interest taken in this work by Prof. A. Ogg and Dr. Lewis Simons, and also my indebtedness to Mr. J. A. Linton for the efficiency with which he constructed the apparatus used in the course of the research.

University of Cape Town,
September 1922.

XL. *Proceedings of Learned Societies.*

GEOLOGICAL SOCIETY.

[Continued from vol. xliv. p. 1062.]

November 8th, 1922.—Prof. A. C. Seward, Sc.D., F.R.S.,
President, in the Chair.

THE following communications were read:—

1. 'The Earthquake of 7th August, 1895, in Northern Italy.
By Richard Dixon Oldham, F.R.S., F.G.S.

This earthquake, although nowhere more than a feeble shock, was felt over an area measuring about 160 miles across and covering some 15,000 to 20,000 square miles in Lombardy and Tuscany. A detailed examination of the reports gives no indication of a central area of greatest intensity; reports indicating an intensity of IV° (Mercalli scale) are scattered over the whole area up to the extreme limits; reports of sounds and of noticeable vertical movement are similarly distributed. The nature of the disturbance was different from that usual in slight earthquakes, and more akin to that noticed in the outer parts of the seismic area of great earthquakes. The reports are discussed, and the conclusion is drawn that the depth of the ultimate origin of the earthquake must have been of the order of 100 miles or more.

2. 'The Pamir Earthquake of 18th February, 1911.' By Richard Dixon Oldham, F.R.S., F.G.S.

This earthquake has been attributed to the fall of a very large landslip, which certainly accompanied it. As a surface-origin of a great earthquake, registered by distant seismographs, is contrary to the trend of our knowledge, the original records of this earthquake have been investigated. These show that it was felt over an area of about 250 miles in diameter, that the region included by the VIII° R.F. isoseist measured about 40 miles across, and that over the greater part of this area destruction was extreme, and the hillsides were scamed with landslips. For all this there must have been a common cause, which is to be found in the earthquake, and this could not have been due to the great landslip, for it lies on the extreme limit, and not near the centre, of the region of destructive violence. Aftershocks were recorded, providing further evidence that the earthquake was of the ordinary type, having its origin at a considerable depth below the surface. It is pointed out that the great landslip, though determined by, and not determining, the earthquake, may have influenced the distant seismograms by setting up surface-waves which, superimposed on those

directly due to the earthquake, may account for the unusual size of the long (or surface-) waves, as compared with the preliminary tremors.

3. 'The Geology of Sierra Leone.' By Frank Dixey, D.Sc., F.G.S.

About half of the Protectorate of Sierra Leone is composed of potash-bearing granites and granite-gneisses, while the remaining areas are occupied equally by older schists and gneisses and the ancient sedimentary Rokell River Series.

The older schists and gneisses, including a charnockitic series similar to that of the Ivory Coast, represent a complex of highly metamorphosed sedimentary and igneous rocks.

The normal granites and gneisses are associated with tourmaline-granites, cancrinite-syenite, alkaline gabbros, and a number of minor intrusions. Basic igneous rocks, of various ages, are represented by the great noritic complex of the Sierra Leone Peninsula, and by a large number of dolerite-dykes that cut the older crystalline rocks and also the horizontal sandstones of the Saionia Scarp Series (presumably of early Palæozoic age).

The Rokell River Series has a lower conglomeratic division that rests unconformably upon the crystalline rocks. Its upper portion is composed of argillaceous and arenaceous sediments, with which are interbedded a series of acid and basic lavas and rhyolitic ashes and tuffs. The rocks of the Rokell River Series are usually much disturbed, and show every gradation from slight deformation to intense dynamic metamorphism.

The southern margin of the great series of horizontal sandstones of French Guinea forms, near the Anglo-French boundary of the Protectorate, the Saionia Scarp, and thus the formation within the Protectorate bears the name Saionia Scarp Series. It rests alike with striking unconformity upon the Rokell River Series and the crystalline rocks.

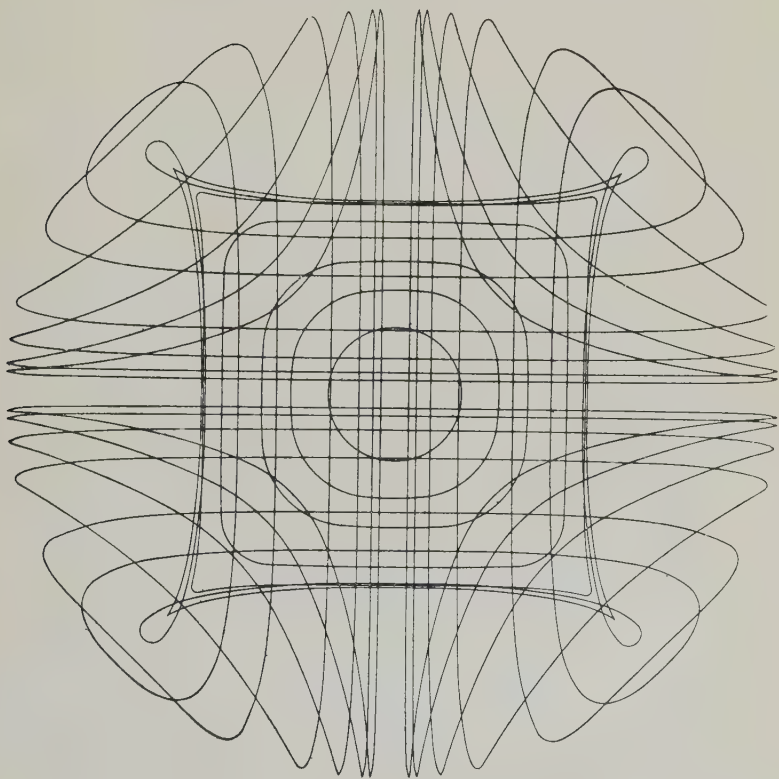
The Plateau Sands, resting upon the crystalline plateaux, are compared with the 'drift' of Northern Nigeria.

November 22nd, 1922.—Prof. A. C. Seward, Sc.D., F.R.S.,
President, in the Chair.

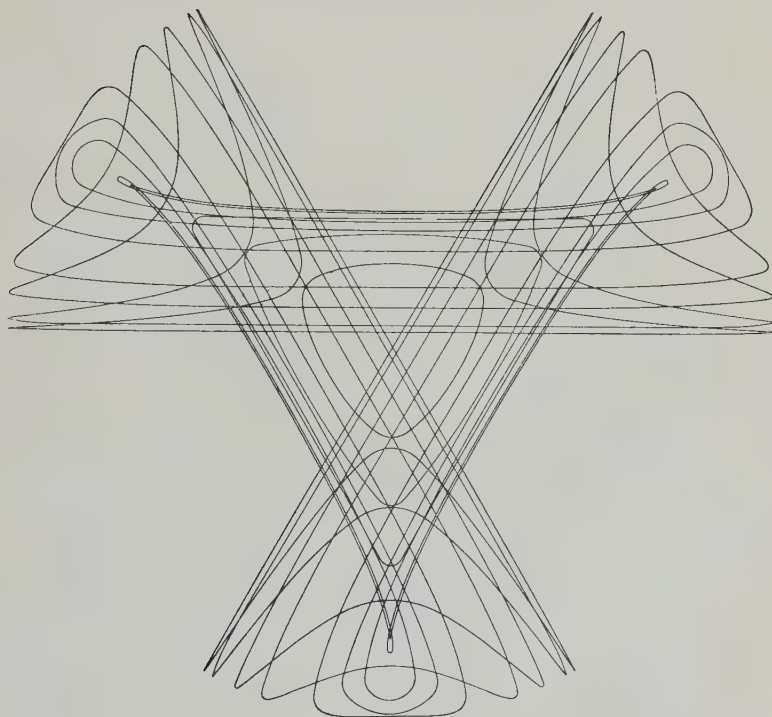
Prof. ARTHUR STANLEY EDDINGTON, M.A., F.R.S., Pres.R.A.S., delivered a lecture on The Borderland of Astronomy and Geology. He considered first, in reference to rival hypotheses as to the origin of the Earth and the solar system, the general evolution of the stellar universe. The trend of modern astronomy is against the view that luminous stars are being formed by collisions of extinct stars (unless very exceptionally); the stars now observed have systematic relations one to the other, apparently indicating that they have been formed as the result of a single

evolutionary process sweeping across the primordial matter. Collisions, in any case, would be extremely rare, since dynamical arguments indicate that extinct stars cannot greatly outnumber the observed luminous stars. Whether the original matter was gaseous or meteoric, it must have become entirely gaseous at a very early stage in the formation of a star: this is inferred from the fact that the masses of stars differ very little one from the other, and agree numerically with a certain critical mass, predicted theoretically for a sphere of gas, but unexplained if the star consisted of a swarm of meteorites. It is supposed that radiation-pressure was instrumental in breaking up the original matter into separate stars. These considerations favour the nebular hypothesis; but, if we accept Jeans's suggestion that the solar system is an exceptional formation, and that undisturbed stars cannot give birth to a planetary system, the argument is less cogent, since it refers only to stars developing normally. Astronomy now demands a great enlargement of Lord Kelvin's time-scale for the age of the sun; the most direct evidence is obtained from Cepheid variables, which are found to be developing at only $1/500$ of the rate which Kelvin's hypothesis assumed. The sun must at one time have given out from 20 to 50 times as much heat as it emits now; but it is uncertain whether any geological strata go back to an epoch when the sun was sensibly hotter than now. Darwin's views on tidal evolution and the origin of the earth-moon system seem to have held their own against all criticism. The present rate of lengthening of the day (deduced from ancient eclipses) is about 1 minute in 6 million years; it is, therefore, difficult to date the birth of the moon later than 1000 million years ago. There seems to be no objection to the postulate that the Earth had a cool solid crust at the time of the catastrophe, if that would explain geological observations; the Pacific Ocean may be the depression which was left, and may have received the waters which formerly covered most of the Earth. The dissipation of energy by the tides occurs chiefly in the land-locked shallow seas, G. I. Taylor having shown that the Irish Sea alone accounts for $1/50$ of the whole amount. The brake on the Earth's rotation is thus a surface-brake; and the hypothesis suggests itself that there may be a slip of the outer crust over the interior at the 'zone of weakness.' If the slip is irregular, this would help to explain certain astronomical observations of irregularities in the longitudes of the moon, sun, and planets. It might even be the cause of the motion of the magnetic poles. The brake, being applied irregularly over the surface, would also tend to crumple the crust. The postulated looseness of the crust might also permit the North Pole to move about over the surface; but exceedingly long periods of time would be required, since there is no systematic tendency of the crust to move in latitude.

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